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# Substrate-controlled divergent synthesis with *ortho*-vinyl-functionalised 1,3-enynes and imines via palladium catalysis

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## Supplementary Information

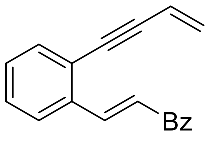
## 1. General methods

Unless otherwise noted, the reactions were carried out under ambient atmosphere; when the reactions required heating, the heat source was oil bath. $^1$H NMR (400 MHz or 600 MHz), $^{13}$C NMR (100 MHz or 150 MHz) and $^{19}$F NMR (375 MHz) spectra were recorded on Varian INOVA 400/54, Agilent DD2 600/54 or Bruker AscendTM 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet doublet, td = triple doublet, dt = double triplet, brs = broad singlet, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on Bruker D8 venture diffractometer, and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2249982–2249984). In each case, enantiomeric excess was determined by HPLC analysis on a chiral stationary phase in comparison with the authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm), Chiralpak IE Column (250 × 4.6 mm), Chiralpak IF Column (250 × 4.6 mm). UV detection was monitored at 254 nm. Column chromatography was performed on silica gel (200–300 mesh) eluting with redistilled EtOAc and petroleum ether. TLC was performed on glass-backed silica plates. UV light (monitored at 254 nm), $I_2$ and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. THF was freshly distilled from sodium/benzophenone before use. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes.

## 2. Substrate preparation and characterization

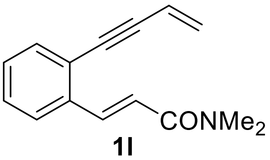
### 2.1 Preparation of 1,3-enyne substrates 1a–1o

1,3-Enynes **1a–1j**, **1m–1o** were prepared according to the literature procedures,[1] which are known compounds and the spectroscopic data are consistent with the literature reports. The characterizations of new substrates are as follows:



**1k**

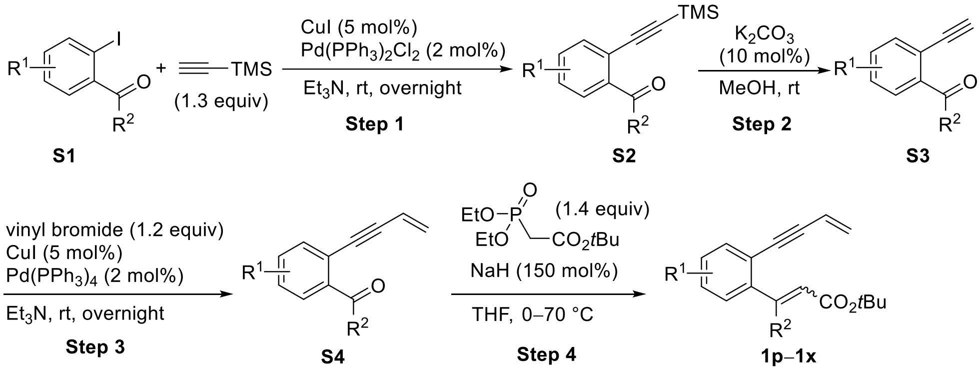
**1k**, obtained as a yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (d, *J* = 15.9 Hz, 1H), 8.09–7.93 (m, 2H), 7.79–7.69 (m, 1H), 7.67–7.55 (m, 2H), 7.55–7.43 (m, 3H), 7.42–7.30 (m, 2H), 6.07 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.77 (dd, *J* = 17.5, 2.0 Hz, 1H), 5.60 (dd, *J* = 11.1, 2.0 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 191.0, 142.9, 138.2, 136.2, 133.1, 132.7, 129.9, 128.61, 128.58, 127.8, 126.7, 124.3, 124.1, 116.9, 94.4, 87.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{14}ONa^+$ 281.0937; Found 281.0930.



**1l**

**1l**, obtained as a white solid, mp = 193–195 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, *J* = 15.5 Hz, 1H), 7.63–7.53 (m, 1H), 7.53–7.43 (m, 1H), 7.36–7.26 (m, 2H), 7.05 (d, *J* = 15.5 Hz, 1H), 6.07 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.79 (dd, *J* = 17.6, 2.0 Hz, 1H), 5.58 (dd, *J* = 11.1, 2.0 Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.7, 140.1, 136.7, 133.1, 128.9, 128.5, 127.6, 126.6, 123.3, 119.6, 117.0, 93.8, 87.9, 37.5, 35.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{15}NONa^+$ 248.1046; Found 248.1053.

### 2.2 Preparation of 1,3-enyne substrates 1p–1x



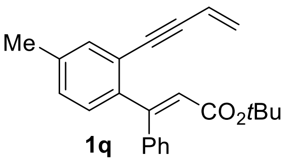
Substrates **S1** were prepared according to the literature procedures and the spectroscopic data of these compounds are consistent with the reports.[2] 1,3-Enyne derivatives **1p–1x** were prepared according to the following procedures:

**Step 1.** To An oven-dried 50 mL flask was charged with $PdCl_2(PPh_3)_2$ (140.0 mg, 0.2000 mmol), CuI (95.0 mg, 0.500 mmol) and **S1** (10.0 mmol). After evacuating and refilling the flask with argon three times, $Et_3N$ (20.0 mL) and ethynyltrimethylsilane (1.82 mL, 13.0 mmol, 1.3 equiv) were added sequentially. The mixture was stirred at room temperature until full consumption of **S1**. The mixture was filtered, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford **S2**.

**Step 2**. **S2** (8.0 mmol, 1.0 equiv) was dissolved in anhydrous MeOH (10 mL) at room temperature. $K_2CO_3$ (110.4 mg, 0.8 mmol, 10 mol%) was added and the mixture was stirred for 10 minutes until complete conversion of **S2**. The reaction was quenched by $H_2O$ and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous $Na_2SO_4$. After concentration, the crude product **S3** was used for the next step directly without further purification.

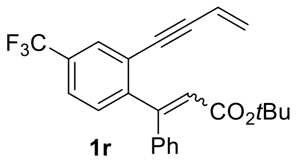
**Step 3.** To an over-dried flask equipped with a stirring bar were added CuI (76 mg, 0.4 mmol, 5 mol%) and $Pd(PPh_3)_4$ (184.8 mg, 0.1600 mmol, 2 mol%). After evacuating and refilling the flask with argon three times, $Et_3N$ (20 mL), crude **S3** (8.0 mmol, 1.0 equiv) and vinyl bromide (1.0 M in THF, 9.6 mL, 9.6 mmol, 1.2 equiv) were added via syringe sequentially. The resulting mixture was stirred at room temperature until complete conversion of **S3**. The mixture was filtered, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford **S4**.

**Step 4.** NaH (300 mg, 7.50 mmol, 1.5 equiv) was suspended in anhydrous THF (15 mL) under atmosphere of argon. *tert*-Butyl diethylphosphonoacetate (1.64 mL, 7.00 mmol, 1.4 equiv) was then added slowly to the suspension over 15 minutes at 0 °C. The mixture was stirred about 30 minutes, and **S4** (6 mmol, 1.0 equiv) was added. Then the reaction was stirred at 70 °C until full consumption of **S4**. After cooled to room temperature, the mixture was quenched with $H_2O$ and extracted with EtOAc (20 mL × 3). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford 1,3-enyne derivatives.



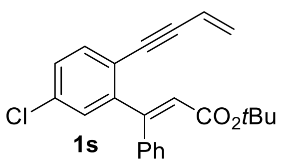
**1q**

**1q**, obtained as a colorless oil; 43% yield for four steps; $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36–7.25 (m, 6H), 7.17–7.11 (m, 1H), 7.02 (d, $J$ = 7.9 Hz, 1H), 6.35 (s, 1H), 5.81 (dd, $J$ = 17.5, 11.1 Hz, 1H), 5.48 (dd, $J$ = 17.5, 2.2 Hz, 1H), 5.39 (dd, *J* = 11.1, 2.2 Hz, 1H), 2.36 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.3, 152.9, 140.7, 139.4, 137.3, 132.5, 129.0, 128.9, 128.3, 127.8, 126.6, 122.3, 121.3, 117.3, 90.8, 89.0, 80.1, 27.8, 21.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{24}O_2Na^+$ 367.1669; Found 367.1677.



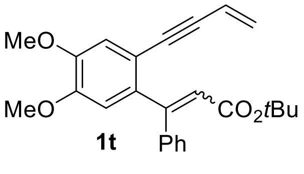
**1r**

**1r**, obtained as a colorless oil; 21% yield for four steps; *E/Z* = 11:1, *E*-**1r**: $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (s, 1H), 7.56 (d, *J* = 8.1 1H), 7.40–7.26 (m, 4H), 7.25–7.19 (m, 2H), 6.42 (s, 1H), 5.82 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.59–5.51 (dd, *J* = 17.5, 2.4 Hz, 1H), 5.51–5.43 (dd, *J* = 11.1, 2.3 Hz, 1H), 1.26 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 164.8, 151.4, 145.9, 139.4, 129.5, 129.3, 128.8 (q, $^4J_{FC}$ = 2.6 Hz), 128.5, 127.9, 127.6, 125.0 (q, $^1J_{FC}$ = 250.1 Hz), 124.4 (q, $^4J_{FC}$ = 2.4 Hz), 123.5, 122.0, 116.7, 92.6, 87.1, 80.6, 77.2, 77.0, 76.8, 27.7; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –62.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{21}F_3O_2Na^+$ 421.1386; Found 421.1378.



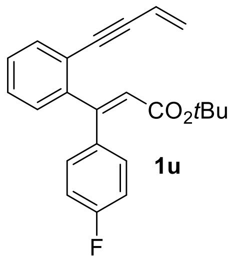
**1s**

**1s**, obtained as a colorless oil; 37% yield for four steps; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (d, *J* = 8.3 Hz, 1H), 7.36–7.25 (m, 6H), 7.15 (d, *J* = 2.2 Hz, 1H), 6.37 (s, 1H), 5.80 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.49 (dd, *J* = 17.6, 2.2 Hz, 1H), 5.42 (dd, *J* = 11.2, 2.2 Hz, 1H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 151.3, 143.9, 139.6, 133.9, 133.0, 129.2, 129.1, 128.5, 127.8, 127.7, 127.3, 122.0, 121.2, 116.9, 92.1, 87.6, 80.5, 27.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}{}^{35}ClO_2Na^+$ 387.1122; Found 387.1115; Calcd for $C_{23}H_{21}{}^{37}ClO_2Na^+$ 389.1093; Found 389.1090.

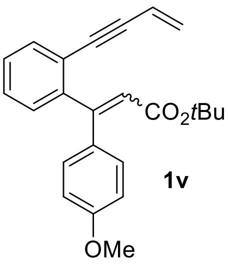


**1t**

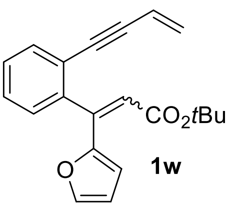
**1t**, obtained as a colorless oil; 23% yield for four steps; *E/Z* = 2.5:1, *E*-**1t**: $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36–7.27 (m, 5H), 6.99 (s, 1H), 6.61 (s, 1H), 6.36 (s, 1H), 5.81 (m, 1H), 5.55–5.34 (m, 2H), 3.91 (s, 3H), 3.81 (s, 3H), 1.32 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.3, 152.4, 149.1, 148.2, 140.5, 135.5, 129.0, 128.3, 127.8, 126.1, 121.4, 117.3, 115.2, 114.8, 114.2, 112.9, 112.1, 89.9, 89.0, 80.1, 55.9, 27.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{26}O_4Na^+$ 413.1723; Found 413.1721.


**1u**

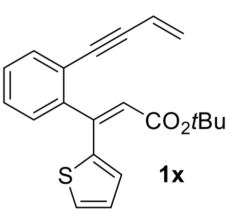
**1u**, obtained as a colorless oil; 19% yield for four steps; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57–7.48 (m, 1H), 7.36–7.29 (m, 2H), 7.30–7.25 (m, 2H), 7.20–7.11 (m, 1H), 7.04–6.93 (m, 2H), 6.35 (s, 1H), 5.85 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.53 (dd, *J* = 17.5, 2.2 Hz, 1H), 5.45 (dd, *J* = 11.0, 2.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.1, 163.2 (d, $^1J_{FC}$ = 247.9 Hz), 151.6, 142.1, 136.5 (d, $^3J_{FC}$ = 3.2 Hz), 132.0, 129. 5 (d, $^3J_{FC}$ = 8.3 Hz), 129.0, 127.8 (d, $^2J_{FC}$ = 32.0 Hz), 126.9, 122.5, 121.2, 117.1, 115.3 (d, $^2J_{FC}$ = 21.5 Hz), 91.4, 88.5, 80.3, 27.7; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –112.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}FO_2Na^+$ 371.1418; Found 371.1419.


**1v**

**1v**, obtained as a colorless oil; 29% yield for four steps; *E/Z* = 3.1:1, *E*-**1v**: $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52–7.45 (m, 1H), 7.33–7.25 (m, 2H), 7.23–7.17 (m, 2H), 7.17–7.10 (m, 1H), 6.87–6.75 (m, 2H), 6.31 (s, 1H), 5.83 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.58–5.46 (m, 1H), 5.46–5.36 (m, 1H), 3.78 (s, 3H), 1.24 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.5, 160.4, 152.3, 142.6, 132.7, 131.9, 131.1, 129.1, 129.0, 127.9, 127.4, 126.7, 122.5, 121.9, 119.4, 117.2, 113.7, 91.1, 88.7, 79.9, 55.3, 27.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{24}O_3Na^+$ 383.1618; Found 383.1626.


**1w**

**1w**, obtained as a colorless oil; 16% yield for four steps; *E/Z* = 3.1:1, *E*-**1w**:$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46–7.36 (m, 2H), 7.25 (m, 2H), 7.17–7.12 (m, 1H), 6.44 (s, 1H), 6.32–6.24 (m, 1H), 5.90 (d, *J* = 3.4 Hz, 1H), 5.85–5.75 (m, 1H), 5.54–5.42 (m, 1H), 5.41–5.31 (m, 1H), 1.16 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.3, 153.5, 144.0, 131.9, 128.8, 127.70, 127.67, 126.9, 117.0, 113.7, 112.0, 91.2, 88.3, 79.9, 27.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_3Na^+$ 343.1305; Found 343.1307.


**1x**

**1x**, obtained as a colorless oil; 35% yield for four steps; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57–7.49 (m, 1H), 7.42–7.31 (m, 3H), 7.28–7.22 (m, 1H), 6.97 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.77 (dd, *J* = 3.8, 1.2 Hz, 1H), 6.43 (s, 1H), 5.88 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.56 (dd, *J* = 17.5, 2.2 Hz, 1H), 5.46 (dd, *J* = 11.1, 2.2 Hz, 1H), 1.26 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.0, 146.2, 144.6, 141.5, 131.9, 129.1, 128.7, 127.82, 127.81, 127.7, 127.4, 127.0, 122.4, 118.6, 117.2, 91.4, 88.3, 80.1, 27.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_2SNa^+$ 359.1076; Found 359.1075.

Substrate imines **2** were synthesized according to the literature procedures, and the spectroscopic data were consistent with the literature reports.[3]

**References:**

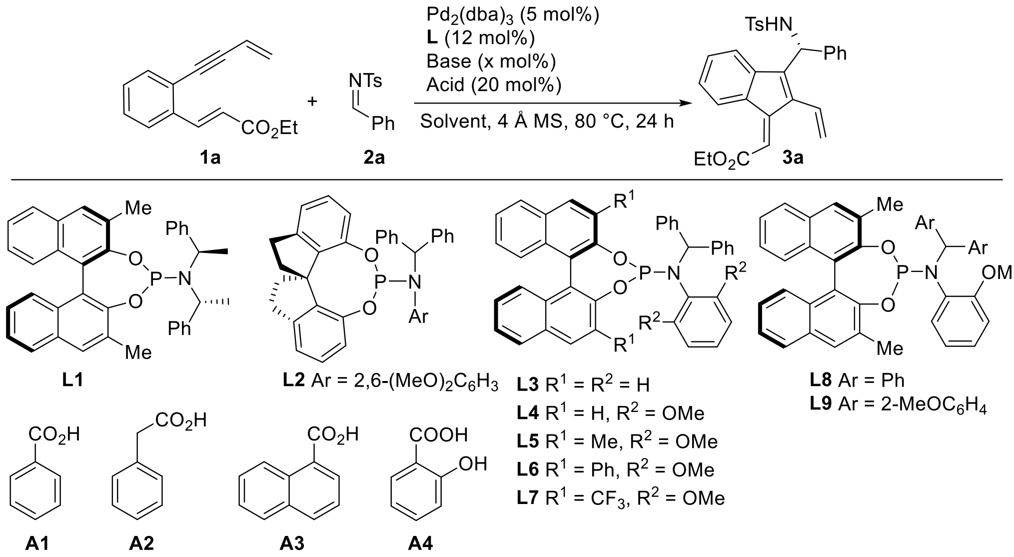
1.R. Huang, B. Yu, R. Li and H. Huang, *Org. Lett.*, 2021, **23**, 9510–9515.

2.X. Hu, Y. Dong and G. Liu, *Mol. Divers.*, 2015, **19**, 695–701.

3. B.-X. Xiao, B. Jiang, R.-J. Yan, J.-X. Zhu, K. Xie, X.-Y. Gao, Q. Ouyang, W. Du and Y.-C. Chen, *J. Am. Chem. Soc.* 2021, **143**, 4809–4816.

# 3. Detailed condition optimization

## 3.1 Detailed screening conditions for asymmetric synthesis of benzofulvene 3a[a]



**L2** Ar = 2,6-(MeO)$_2$C$_6$H$_3$

**L3** R$^1$ = R$^2$ = H
**L4** R$^1$ = H, R$^2$ = OMe
**L5** R$^1$ = Me, R$^2$ = OMe
**L6** R$^1$ = Ph, R$^2$ = OMe
**L7** R$^1$ = CF$_3$, R$^2$ = OMe

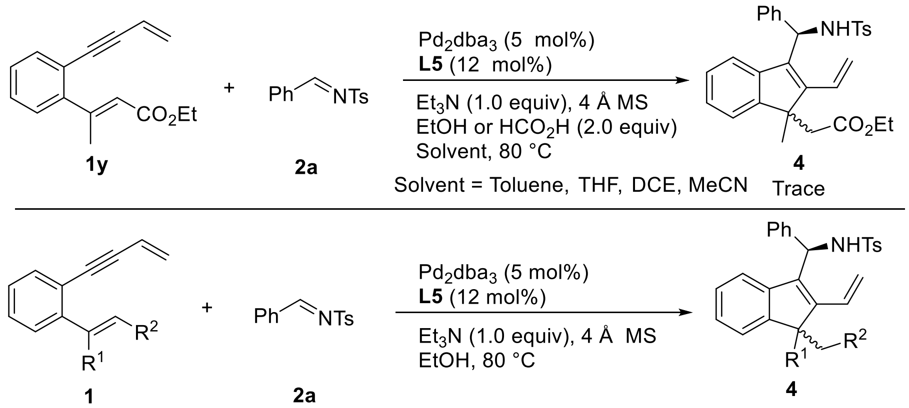
**L8** Ar = Ph
**L9** Ar = 2-MeOC$_6$H$_4$

| Entry | L | Base | x | *Temp* (°C) | *t* (h) | Acid | Solvent | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|---|---|---|---|---|
| 1[d] | – | Et$_3$N | 100 | 80 | 24 | – | EtOH | NR | – |
| 2 | **L1** | Et$_3$N | 100 | 80 | 24 | – | EtOH | NR | – |
| 3 | **L2** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 10 | 56 |
| 4 | **L3** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 38 | 37 |
| 5 | **L4** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 56 | 70 |
| 6 | **L5** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 71 | 84 |
| 7 | **L6** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 20 | 76 |
| 8 | **L7** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 67 | 83 |
| 9 | **L8** | Et$_3$N | 100 | 80 | 24 | – | EtOH | 73 | 81 |
| 10 | **L9** | Et$_3$N | 100 | 80 | 24 | – | EtOH | trace | 90 |
| 11 | **L5** | Et$_3$N | 0 | 80 | 24 | – | EtOH | trace | – |
| 12 | **L5** | Et$_3$N | 20 | 80 | 24 | – | EtOH | 34 | 83 |
| 13 | **L5** | Et$_3$N | 200 | 80 | 24 | – | EtOH | 65 | 84 |
| 14 | **L5** | DIPEA | 100 | 80 | 24 | – | EtOH | 63 | 82 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 15 | **L5** | $K_2CO_3$ | 100 | 80 | 24 | – | EtOH | trace | – |
| 16 | **L5** | $Et_3N$ | 100 | 80 | 24 | – | Toluene | 47 | 65 |
| 17 | **L5** | $Et_3N$ | 100 | 80 | 24 | – | THF | 56 | 68 |
| 18 | **L5** | $Et_3N$ | 100 | 80 | 24 | – | *i*-PrOH | 84 | 73 |
| 19 | **L5** | $Et_3N$ | 100 | 60 | 48 | – | EtOH | 73 | 88 |
| 20 | **L5** | $Et_3N$ | 100 | 50 | 60 | – | EtOH | 73 | 90 |
| 21 | **L5** | $Et_3N$ | 100 | 40 | 96 | – | EtOH | 80% conv | 92 |
| 22 | **L5** | $Et_3N$ | 100 | 50 | 60 | **A1** | EtOH | 87 | 91 |
| 23 | **L5** | $Et_3N$ | 100 | 50 | 60 | **A2** | EtOH | 90% conv | 91 |
| 24 | **L5** | $Et_3N$ | 100 | 50 | 60 | **A3** | EtOH | 85 | 91 |
| 25 | **L5** | $Et_3N$ | 100 | 50 | 60 | **A4** | EtOH | 76 | 91 |
| 26[e] | **L5** | $Et_3N$ | 100 | 50 | 60 | **A1** | EtOH | 84 | 91 |
| 27[f] | **L5** | $Et_3N$ | 100 | 50 | 60 | **A1** | EtOH | 63 | 91 |

[a] Unless noted otherwise, reactions were performed with **1a** (0.05 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (5 mol%), **L** (12 mol%), base (x mol%), acid (20 mol%) and 4 Å MS (30 mg) in degassed dry solvent (0.5 mL) under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis using a chiral stationary phase. [d] With $Pd(PPh_3)_4$ (10 mol%). [e] **L5** (20 mol%). [f] $Pd_2(dba)_3$ (2.5 mol%), **L5** (6 mol%)

## 3.2 Detailed screening conditions for asymmetric synthesis of indene derivative 4

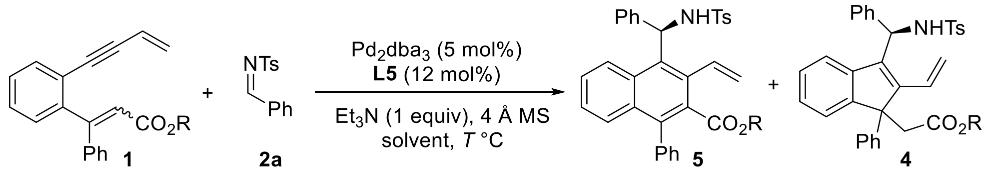


$R^1$ = Me, $R^2$ = H, NR
$R^1$ = Me, $R^2$ = CN, trace
$R^1$ = Me, $R^2$ = Ph (*E/Z* = 2:1), bad conv

$R^1$ = $CO_2Et$, $R^2$ = H, NR
$R^1$ = Me, $R^2$ = $CO_2$*t*Bu, 70% conv, 2:1 dr
$R^1$ = *i*Pr, $R^2$ = $CO_2Et$, 60% conv, 65:35 dr

To improve the diastereoselectivity for asymmetric synthesis of **4**, a series of solvents, enyne substrates and reductants were screened, but inferior results were generally obtained.

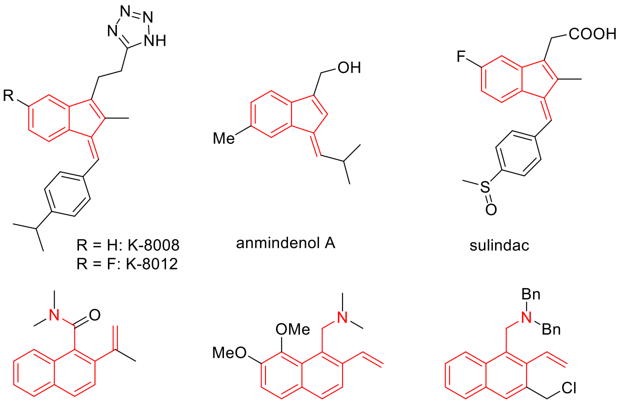
## 3.3 Detailed screening conditions for asymmetric synthesis of naphthalene 5[a]



| Entry | R | Solvent | *T*emp (°C) | Time (h) | Yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|---|---|
| 1 | Et | EtOH | 80 | 24 | **5r**, 45<br>**4b**, 15 | 57[d]<br>63 |
| 2 | Et | Dioxane | 80 | 24 | **5r**, 59 | 61 |
| 3 | Bn | Dioxane | 80 | 24 | **5s**, 47 | 66 |
| 4 | *t*Bu | Dioxane | 80 | 24 | **5a**, 66 | 73 |
| 5[e] | *t*Bu | Dioxane | 80 | 24 | **5a**, 68 | 70 |
| 6 | *t*Bu | Dioxane | 60 | 48 | **5a**, 67 | 79 |
| 7[f] | *t*Bu | Dioxane | 60 | 48 | **5a**, 43 | 80 |
| 8 | *t*Bu | Dioxane | 50 | 60 | **5a**, 63 | 82 |
| 9 | *t*Bu | EtOH | 50 | 60 | **5a**, 81 | 82 |
| 10 | *t*Bu | *i*-PrOH | 50 | 60 | **5a**, 78 | 81 |

[a] Unless noted otherwise, when R is tert butyl, the substrate is a single E-configuration. The reactions were performed with **1** (0.05 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (5 mol%), **L5** (12 mol%), $Et_3N$ (1.0 equiv) and 4 Å MS (30 mg) in solvent (0.5 mL) at 80 ℃ under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis using a chiral stationary phase. [d] The structure of racemic **5r** has been determined by X-ray analysis. [e] *E/Z* = 3:1. [f] Without $Et_3N$.

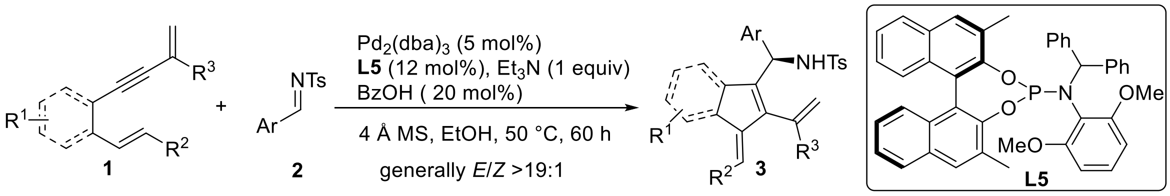
### 3.4 Selected molecules embedding a benzofulvene or 1-naphthylated amine skeleton



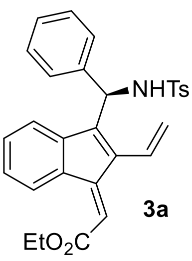
(*a*) *Chemistry & Biology.*, 2014, **21**, 601; (*b*) *J. Med. Chem.*, 2008, **51**, 4911; (*c*) *J. Org. Chem.*, 2019, **84**, 10953; (*d*) *Org. Lett.*, 2020, **22**, 8962.

Benzofulvenes, as a class of important skeleton, are widely existed in various natural products and bioactive molecules. As briefly exemplified in the above scheme, Zhang's group disclosed that **K-8008** and **K-8012** are able to induce tumor apoptosis. Anmindenol A, separated from a marine-derived bacterium Streptomyces sp. in 2014, is a potential nitric oxide synthase inhibitor. In addition, Sulindac is widely used as a non-steroidal anti-inflammatory drug. In addition, the *ortho*-vinylated 1-naphthylated amines can be used as ligands in asymmetric transition-metal catalysis.

## 4. General procedure for asymmetric synthesis of benzofulvenes 3

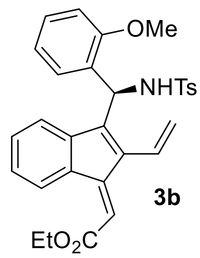


To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *ortho*-vinyl-functionalized 1,3-enyne **1** (0.100 mmol), imine **2** (0.200 mmol), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give benzofulvene **3**.



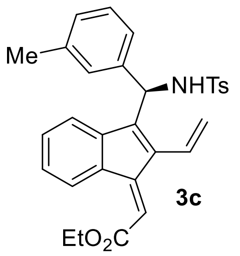
**3a**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), **L5** (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3a**: 42.0 mg (0.0866 mmol), as a yellow solid; 87% yield; mp = 123–125 ℃; $[\alpha]_D^{25}$ = +131.1 (*c* = 0.33 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.19 min (minor), $t_R$ = 7.61 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.43–8.38 (m, 1H), 7.47–7.36 (m, 4H), 7.34–7.25 (m, 3H), 7.16–7.02 (m, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.78 (dd, *J* = 7.0, 1.3 Hz, 1H), 6.32 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.24 (s, 1H), 5.92 (d, *J* = 9.0 Hz, 1H), 5.54 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.46 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.19 (dd, *J* = 17.8, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.0, 149.8, 143.3, 141.6, 140.6, 138.5, 138.1, 136.6, 133.2, 129.8, 128.92, 128.85, 128.0, 127.6, 127.1, 126.91, 126.89, 126.7, 122.6, 120.4, 119.1, 60.9, 53.9, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{29}H_{27}NO_4SNa^+$ 508.1553; Found 508.1555.



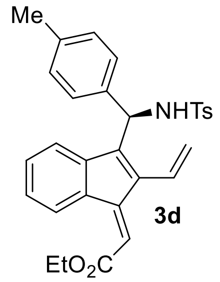
3b

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(2-methoxybenzylidene)-4-methylbenzenesulfonamide **2b** (59.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **3b**: 45.7 mg (0.0886 mmol), as a yellow solid, 89% yield; mp = 57–59 ℃; $[\alpha]_D^{25}$ = +13.1 (*c* = 0.52 in CHCl$_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: t$_R$ = 9.56 min (minor), t$_R$ = 13.55 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.45–8.34 (m, 1H), 7.56–7.47 (m, 2H), 7.32–7.27 (m, 1H), 7.26–7.18 (m, 2H), 7.15–7.06 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.86–6.77 (m, 2H), 6.49 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.33 (s, 1H), 5.99 (d, *J* = 5.4 Hz, 1H), 5.45 (dd, *J* = 11.5, 1.8 Hz, 1H), 5.33–5.25 (m, 1H), 5.10 (dd, *J* = 17.8, 1.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.70 (s, 3H), 2.28 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 166.3, 156.7, 150.0, 143.1, 142.7, 141.1, 137.7, 136.5, 133.0, 129.64, 129.55, 128.9, 128.6, 128.2, 127.4, 126.6, 126.5, 125.9, 122.3, 121.3, 120.6, 119.1, 110.8, 60.9, 55.3, 51.1, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{30}H_{29}NO_5SNa^+$ 538.1659; Found 538.1666.



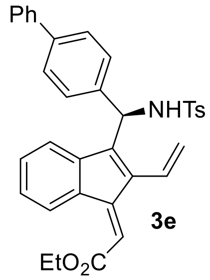
3c

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide **2c** (54.6 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 0.0050 mmol, 5 mol%), **L5** (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3c**: 35.8 mg (0.0717 mmol), as a yellow solid, 72% yield; mp = 135−137 °C; $[\alpha]_D^{25}$ = +152.3 (*c* = 0.26 in $CHCl_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.41 min (minor), $t_R$ = 6.13 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.44–8.37 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.25–7.23 (m, 1H), 7.18–7.03 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.81–6.76 (m, 1H), 6.33 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.24 (s, 1H), 5.89 (d, *J* = 9.2 Hz, 1H), 5.52–5.42 (m, 2H), 5.20 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.0, 149.9, 143.3, 141.7, 140.7, 138.7, 138.4, 138.0, 136.6, 133.2, 129.8, 128.9, 128.8, 128.7, 127.6, 127.3, 127.0, 126.9, 123.7, 122.6, 120.4, 119.0, 60.9, 53.9, 21.5, 21.3, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710; Found 522.1718.



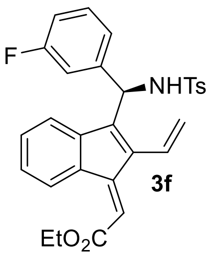
**3d**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide **2d** (54.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), **L5** (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3d**: 44.7 mg (0.0896 mmol), as a yellow solid, 90% yield; mp = 140−142 °C; $[\alpha]_D^{25}$ = +104.3 (*c* = 0.40 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.75 min (minor), $t_R$ = 8.43 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.43–8.37 (m, 1H), 7.45–7.37 (m, 2H), 7.31–7.27 (m, 2H), 7.16–7.06 (m, 4H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.80–6.74 (m, 1H), 6.31 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.23 (s, 1H), 5.87 (d, *J* = 8.9 Hz, 1H), 5.46 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.36–5.27 (m, 1H), 5.18 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.0, 149.9, 143.3, 141.7, 140.7, 138.4, 137.9, 136.6, 135.1, 133.2, 129.7, 129.5, 128.9, 127.6, 127.1, 126.89, 126.87, 126.7, 122.5, 120.5, 119.0, 60.9, 53.8, 21.4, 21.1, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710; Found 522.1715.



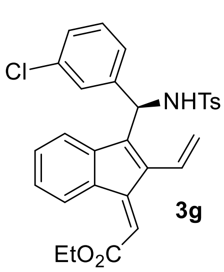
**3e**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-([1,1'-biphenyl]-4-ylmethylene)-4-methylbenzenesulfon amide **2e** (67.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), **L5** (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3e**: 48.3 mg (0.0861 mmol), as a yellow solid, 86% yield; mp = 71–73 °C; $[\alpha]_D^{25} = +66.7$ ($c = 0.17$ in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.64 min (minor), $t_R$ = 10.94 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.45–8.38 (m, 1H), 7.58–7.46 (m, 6H), 7.46–7.38 (m, 4H), 7.36–7.30 (m, 1H), 7.17–7.06 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.83 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.34 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.26 (s, 1H), 5.96 (d, *J* = 9.0 Hz, 1H), 5.59–5.52 (m, 1H), 5.48 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.22 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.0, 149.8, 143.4, 141.6, 141.0, 140.5, 140.4, 138.6, 137.1, 136.6, 133.2, 129.8, 129.0, 128.8, 127.6, 127.54, 127.51, 127.21, 127.16, 127.1, 127.0, 126.9, 122.7, 120.5, 119.2, 61.0, 53.8, 21.4, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{31}NO_4SNa^+$ 584.1866; Found 584.1875.



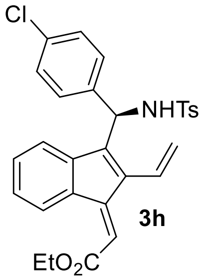
**3f**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(3-fluorobenzylidene)-4-methylbenzenesulfonamide **2f** (55.4 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3f**: 37.8 mg (0.0751 mmol), as a yellow solid, 75% yield; mp = 114–116 °C; $[\alpha]_{D}^{25}$ = +123.6 (*c* = 0.39 in CHCl$_3$); 83% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.78 min (minor), $t_R$ = 11.62 min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.41 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.45–7.39 (m, 2H), 7.31–7.24 (m, 1H), 7.22–7.05 (m, 4H), 7.00–6.91 (m, 3H), 6.75 (dd, *J* = 7.0, 1.4 Hz, 1H), 6.27 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.25 (s, 1H), 5.88 (d, *J* = 9.1 Hz, 1H), 5.61–5.54 (m, 1H), 5.48 (dd, *J* = 11.5, 1.5 Hz, 1H), 5.19 (dd, *J* = 17.8, 1.5 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 165.9, 163.1 (d, $^1J_{FC}$ = 245.4 Hz), 149.6, 143.5, 141.2, 141.0 (d, $^3J_{FC}$ = 7.0 Hz), 139.9, 138.7, 136.5, 133.1, 130.4 (d, $^3J_{FC}$ = 8.2 Hz),, 129.8, 129.0, 127.5, 127.3, 127.1, 126.9, 122.8, 122.3, 120.2, 119.6, 115. 1 (d, $^2J_{FC}$ = 21.0 Hz), 113. 9 (d, $^2J_{FC}$ = 23.0 Hz), 61.0, 53.5 (d, $^4J_{FC}$ = 2.0 Hz), 21.4, 14.3; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ (ppm) –111.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{29}H_{26}FNO_4SNa^+$ 526.1459; Found 526.1467.



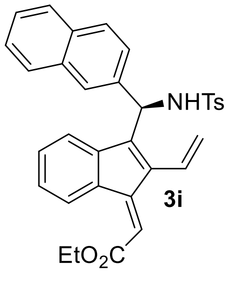
**3g**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(3-chlorobenzylidene)-4-methylbenzenesulfonamide **2g** (58.6 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3g**: 39.9 mg (0.0767 mmol), as a yellow solid, 77% yield; mp = 128–130 °C; $[\alpha]_{D}^{25}$ = +112.1 (*c* = 0.38 in CHCl$_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.77 min (minor), $t_R$ = 11.60 min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 8.48–8.36 (m, 1H), 7.49–7.36 (m, 3H), 7.32–7.20 (m, 3H), 7.20–7.07 (m, 2H), 7.00–6.91 (m, 2H), 6.80–6.70 (m, 1H), 6.28 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.25 (s, 1H), 5.86 (d, *J* = 9.1 Hz, 1H), 5.54–5.43 (m, 2H), 5.19 (dd, *J* = 17.7, 1.5 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 165.9, 149.5, 143.5, 141.2, 140.4, 139.7, 138.8, 136.5, 134.9, 133.1, 130.1, 129.9, 129.1, 128.3, 127.5, 127.3, 127.1, 126.89, 126.85, 124.9, 122.9, 120.1, 119.6, 61.0, 53.5, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163; Found 542.1158; Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134; Found 544.1133.



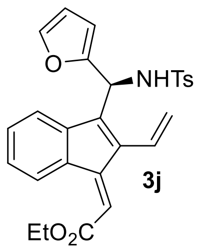
**3h**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **2h** (58.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), **L5** (7.9 mg, 0.012 mmol, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3h**: 44.4 mg (0.0853 mmol), as a yellow solid, 85% yield; mp = 145–147 °C; $[\alpha]_D^{25}$ = +124.1 (*c* = 0.54 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.77 min (minor), $t_R$ = 8.46 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.44–8.36 (m, 1H), 7.44–7.39 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.24 (m, 2H), 7.05–7.17 (m, 2H), 6.98–6.89 (m, 2H), 6.78–6.70 (m, 1H), 6.32–6.24 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.24 (s, 1H), 5.85 (d, *J* = 9.2 Hz, 1H), 5.57–5.50 (m, 1H), 5.47 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.16 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.9, 149.5, 143.5, 141.2, 139.9, 138.7, 136.8, 136.5, 134.0, 133.1, 129.8, 129.01, 128.99, 128.96, 128.2, 127.5, 127.2, 127.1, 126.9, 122.8, 120.2, 119.5, 61.0, 53.4, 21.3, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{29}H_{26}NO_4S^{35}ClNa^+$ 542.1163; Found 542.1172; Calcd for $C_{29}H_{26}NO_4S^{37}ClNa^+$ 544.1134; Found 544.1140.



**3i**

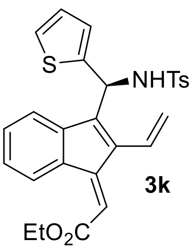
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), imine (*E*)-4-methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide **2i** (61.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3i**: 43.0 mg (0.0802 mmol), as a yellow solid, 80% yield; mp = 149–151 ℃; $[\alpha]^{25}_{D}$ = +127.9 (*c* = 0.43 in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.18 min (minor), $t_R$ = 9.49 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.42 (d, *J* = 7.6 Hz, 1H), 7.86–7.75 (m, 3H), 7.76–7.67 (m, 1H), 7.54 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.48–7.39 (m, 4H), 7.15–7.09 (m, 1H), 7.08–7.01 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 1H), 6.35 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.27 (s, 1H), 6.07 (d, *J* = 9.2 Hz, 1H), 5.62 (d, *J* = 9.2 Hz, 1H), 5.47 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.22 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.0, 149.8, 143.4, 141.7, 140.4, 138.7, 136.6, 135.6, 133.22, 133.18, 133.0, 129.8, 129.0, 128.8, 128.2, 127.6, 127.1, 127.0, 126.9, 126.41, 126.38, 125.5, 124.7, 122.8, 120.4, 119.2, 61.0, 54.2, 21.4, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{29}NO_4SNa^+$ 558.1870; Found 558.1868.



**3j**

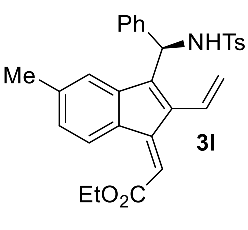
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide **2j** (49.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3j**: 35.4 mg (0.0744 mmol), as a yellow solid, 74% yield; mp = 76–78 ℃; $[\alpha]^{25}_{D}$ = +115.9 (*c* = 0.29 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.29 min (minor), $t_R$ = 9.44 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.43–8.36 (m, 1H), 7.48–7.41 (m, 2H), 7.36–7.30 (m, 1H), 7.18–7.06 (m, 3H), 6.96–6.90 (m, 2H), 6.41 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.31–6.21 (m, 3H), 5.92 (dd, *J* = 7.2, 1.1 Hz, 1H), 5.56 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.44–5.36 (m, 1H), 5.33 (dd, *J* = 17.7, 1.7 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.25

(s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.9, 150.4, 149.8, 143.3, 142.8, 141.5, 138.8, 138.5, 136.4, 132.9, 129.7, 128.9, 127.5, 127.00, 126.96, 126.8, 123.2, 120.5, 119.4, 110.6, 108.2, 60.9, 49.4, 21.3, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{25}NO_5SNa^+$ 498.1346; Found 498.1353.



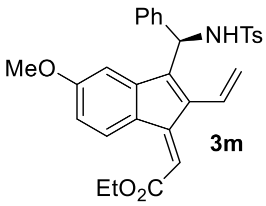
**3k**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1a** (22.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide **2k** (53.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3k**: 40.2 mg (0.0817 mmol), as a yellow solid, 82% yield; mp = 147–149 ℃; $[\alpha]_{D}^{25}$ = +110.4 (*c* = 0.48 in $CHCl_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.31 min (minor), $t_R$ = 8.58 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.45–8.34 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.25–7.22 (m, 1H), 7.17–7.06 (m, 2H), 6.98–6.85 (m, 5H), 6.36 (dd, *J* = 17.7, 11.4 Hz, 1H), 6.25 (s, 1H), 6.04 (d, *J* = 8.9 Hz, 1H), 5.63 (d, *J* = 8.8 Hz, 1H), 5.53 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.30 (dd, *J* = 17.7, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.9, 149.8, 143.5, 142.1, 141.3, 139.9, 138.5, 136.4, 133.1, 129.8, 128.9, 127.4, 127.19, 127.17, 127.0, 126.9, 125.9, 125.6, 122.9, 120.4, 119.5, 61.0, 51.2, 21.4, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{25}NO_4S_2Na^+$ 514.1117; Found 514.1120.



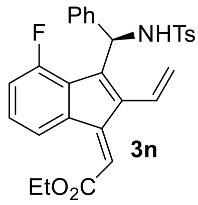
**3l**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)acrylate **1b** (24.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3l**: 42.7 mg (0.0854 mmol), as a yellow thick oil, 85% yield; $[\alpha]_D^{25}$ = +100.0 (*c* = 0.57 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.73 min (minor), $t_R$ = 10.09 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (d, *J* = 7.9 Hz, 1H), 7.46–7.38 (m, 4H), 7.35–7.26 (m, 3H), 7.00–6.86 (m, 3H), 6.58 (s, 1H), 6.26 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.17 (s, 1H), 5.88 (d, *J* = 9.0 Hz, 1H), 5.58–5.46 (m, 1H), 5.43 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.15 (dd, *J* = 17.8, 1.6 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 2.21 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 150.0, 143.3, 142.1, 140.6, 140.2, 138.8, 138.3, 136.6, 130.5, 128.9, 128.8, 128.0, 127.7, 127.5, 127.1, 126.9, 126.8, 122.4, 121.28, 121.26, 118.1, 60.8, 53.9, 21.7, 21.3, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710; Found 522.1720.



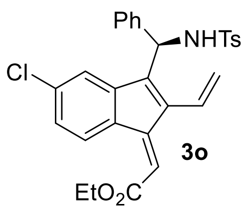
**3m**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-4-methoxyphenyl)acrylate **1c** (25.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and backfilled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **3m**: 44.6 mg (0.0865 mmol), as a yellow solid, 87% yield; mp = 59–61 ℃; $[\alpha]_D^{25}$ = +117.2 (*c* = 0.57 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.08 min (major), $t_R$ = 11.50 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.44 (d, *J* = 8.6 Hz, 1H), 7.51–7.36 (m, 4H), 7.36–7.22 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.59 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.35–6.21 (m, 2H), 6.12 (s, 1H), 5.88 (d, *J* = 8.8 Hz, 1H), 5.50–5.40 (m, 2H), 5.17 (dd, *J* = 17.8, 1.6 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 2.26 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.2, 161.1, 149.9, 143.9, 143.3, 140.1, 139.9, 138.2, 136.7, 129.0, 128.9, 128.0, 127.7, 126.9, 126.7, 125.8, 122.6, 117.0, 109.9, 108.1, 60.7, 55.5, 53.9, 21.4, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NO_5SNa^+$ 538.1659; Found 538.1659.



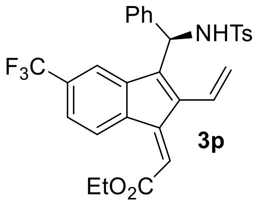
**3n**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-3-fluorophenyl)acrylate **1d** (24.4 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3n**: 32.9 mg (0.0655 mmol), as a yellow solid, 66% yield; mp = 108−110 °C; $[\alpha]_D^{25}$ = +141.4 (*c* = 0.35 in $CHCl_3$); 92% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.58 min (minor), $t_R$ = 10.86 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, *J* = 7.6 Hz, 1H), 7.48–7.20 (m, 7H), 7.17–7.06 (m, 1H), 6.87–6.76 (m, 3H), 6.47 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.36 (s, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.66–5.44 (m, 2H), 5.28 (dd, *J* = 17.7, 1.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.19 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 154.5 (d, $^1J_{FC}$ = 243.8 Hz), 148.9, 148.8, 139.5, 138.4 (d, $^3J_{FC}$ = 5.8 Hz), 138.1, 137.0, 135.9 (d, $^3J_{FC}$ = 6.1 Hz), 128.8, 128.7, 128.7, 128.7, 127.9, 127.2 (d, $^2J_{FC}$ = 14.2 Hz), 127.0, 126.5, 126.4, 123.6, 123.3 (d, $^4J_{FC}$ = 2.4 Hz), 120.6 (d, $^4J_{FC}$ = 1.9 Hz), 117.7 (d, $^2J_{FC}$ = 21.6 Hz), 61.1, 53.7, 21.2, 14.3; $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –111.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{26}FNO_4SNa^+$ 526.1459; Found 526.1468.



**3o**

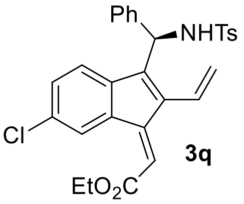
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-4-chlorophenyl)acrylate **1e** (26.1 mg, 0.100 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3o**: 32.7 mg (0.0628 mmol), as a yellow solid, 63% yield; mp = 72–74 ℃; $[\alpha]_D^{25}$ = +53.1 (*c* = 0.34 in $CHCl_3$); 84% ee, determined by HPLC analysis [Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.45 min (major), $t_R$ = 8.48 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.38 (d, *J* = 8.3 Hz, 1H), 7.47–7.40 (m, 2H), 7.38–7.28 (m, 5H), 7.08 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.98–6.91 (m, 2H), 6.76 (d, *J* = 1.9 Hz, 1H), 6.38 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.29 (s, 1H), 5.90 (d, *J* = 8.0 Hz, 1H), 5.53 (dd, *J* = 11.5, 1.5 Hz, 1H), 5.35–5.28 (m, 1H), 5.22 (dd, *J* = 17.8, 1.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 148.8, 143.7, 143.4, 140.1, 139.7, 137.7, 136.5, 135.6, 131.3, 129.1, 129.0, 128.3, 128.1, 127.3, 127.0, 126.7, 126.4, 123.4, 120.8, 119.9, 61.1, 54.0, 21.3, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163; Found 542.1170; Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134; Found 544.1138.



**3p**

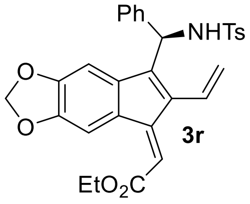
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-4-(trifluoromethyl)phenyl)acrylate **1f** (29.4 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3p**: 35.6 mg (0.0643 mmol), as a yellow solid, 64% yield; mp = 114–116 ℃; $[\alpha]_D^{25}$ = +57.0 (*c* = 0.17 in $CHCl_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 0/10, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 4.42 min (major), $t_R$ = 5.58 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.50 (d, *J* = 8.1 Hz, 1H), 7.44–7.27 (m, 8H), 7.03 (s, 1H), 6.91–6.82 (d, *J* = 8.0 Hz, 2H), 6.47 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.41 (s, 1H), 5.98 (d, *J* = 7.5 Hz, 1H), 5.59 (dd, *J* = 11.5, 1.5 Hz, 1H), 5.33–5.28 (d, *J* = 8.0 Hz, 1H), 5.27 (dd, *J* = 17.8, 1.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.6, 148.3, 143.4, 142.4, 140.1, 139.9, 137.5, 136.4, 136.0, 131.2 (q, $^2J_{FC}$ = 31.9 Hz), 129.1, 128.9, 128.5, 127.2, 126.9, 126.8, 126.7, 126.5

(q, $^{1}J_{FC}$ = 271.0 Hz), 123.8, 123.7 (q, $^{3}J_{FC}$ = 3.9 Hz), 121.5, 116.9 (q, $^{3}J_{FC}$ = 3.8 Hz), 61.3, 54.0, 21.3, 14.3; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –62.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{26}F_3NO_4SNa^+$ 576.1427; Found 576.1436.



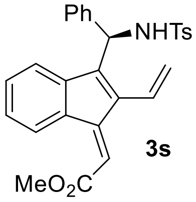
**3q**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-5-chlorophenyl)acrylate **1g** (26.1 mg, 0.100 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3q**: 37.5 mg (0.0721 mmol), as a yellow solid, 72% yield; mp = 121–123 ℃; $[\alpha]_D^{25}$ = +122.2 (*c* = 0.36 in $CHCl_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.48 min (minor), $t_R$ = 7.25 min (major); $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.46 (d, *J* = 2.0 Hz, 1H), 7.44–7.27 (m, 7H), 7.07–7.00 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.35 (dd, *J* = 17.8, 11.5 Hz, 1H), 6.30 (s, 1H), 5.92 (d, *J* = 8.4 Hz, 1H), 5.51 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.48–5.36 (m, 1H), 5.21 (dd, *J* = 17.7, 1.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.7, 148.8, 143.5, 140.0, 139.0, 137.7, 136.5, 134.6, 132.9, 129.3, 128.98, 128.95, 128.3, 127.6, 127.3, 126.9, 126.6, 123.1, 121.2, 120.4, 61.2, 53.9, 21.4, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163; Found 542.1172; Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134; Found 544.1138.



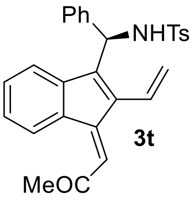
**3r**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(6-(but-3-en-1-yn-1-yl)benzo[*d*][1,3]dioxol-5-yl)acrylate **1h** (27.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 3/1) to give product **3r**: 42.4 mg (0.0800 mmol), as a yellow solid, 80% yield; mp = 58–60 ℃; $[\alpha]_D^{25}$ = +160.0 (*c* = 0.41 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 10.00 min (minor), $t_R$ = 14.54 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (s, 1H), 7.51–7.44 (m, 2H), 7.42–7.35 (m, 2H), 7.34–7.26 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.38–6.22 (m, 2H), 6.16 (s, 1H), 5.96–5.77 (m, 3H), 5.47–5.34 (m, 2H), 5.13 (dd, *J* = 17.7, 1.7 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.0, 149.7, 148.6, 146.7, 143.4, 139.8, 138.0, 137.7, 137.3, 136.7, 129.0, 128.9, 128.1, 127.5, 127.1, 127.0, 126.7, 121.9, 118.5, 109.2, 102.1, 101.5, 60.9, 53.9, 21.4, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{27}NO_6SNa^+$ 552.1451; Found 552.1458.



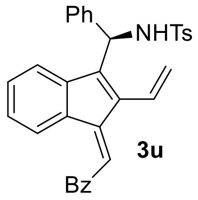
**3s**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added methyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)acrylate **1i** (21.2 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3s**: 31.3 mg (0.0663 mmol), as a yellow solid, 66% yield; mp = 145–147 ℃; $[\alpha]_D^{25}$ = +126.4 (*c* = 0.56 in $CHCl_3$); 87% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.49 min (minor), $t_R$ = 8.25 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.40 (d, *J* = 7.3, 1H), 7.44–7.38 (m, 4H), 7.34–7.26 (m, 3H), 7.17–7.04 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.31 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.25 (s, 1H), 5.91 (d, *J* = 8.9 Hz, 1H), 5.51–5.39 (m, 2H), 5.19 (dd, *J* = 17.7, 1.6 Hz, 1H), 3.86 (s, 3H), 2.25 (s, 3H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 166.3, 150.1, 143.3, 141.6, 140.7, 138.4, 138.1, 136.6, 133.1, 129.8, 128.9, 128.8, 128.0, 127.5, 127.1, 127.0, 126.9, 126.7, 122.6, 120.4, 118.5, 53.9, 51.9, 21.3; HRMS (ESI-TOF) m/z: $[M +H]^+$ Calcd for $C_{28}H_{26}NO_4S^+$ 472.1577; Found 472.1586.



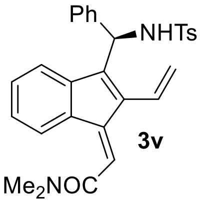
**3t**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added (*E*)-4-(2-(but-3-en-1-yn-1-yl)phenyl)but-3-en-2-one **1j** (19.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3t**: 28.7 mg (0.0631 mmol), as a yellow solid, 63% yield; mp = 162–164 ℃; $[\alpha]_D^{25}$ = +126.6 (*c* = 0.43 in $CHCl_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.90 min (minor), $t_R$ = 9.49 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.29–8.09 (m, 1H), 7.47–7.36 (m, 4H), 7.35–7.26 (m, 3H), 7.14–7.01 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.81–6.73 (m, 1H), 6.53 (s, 1H), 6.34 (dd, *J* = 17.8, 11.4 Hz, 1H), 5.92 (d, *J* = 8.8 Hz, 1H), 5.58–5.41 (m, 2H), 5.19 (dd, *J* = 17.8, 1.6 Hz, 1H), 2.43 (s, 3H), 2.26 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 199.3, 147.2, 143.3, 141.5, 141.4, 138.5, 138.1, 136.6, 133.2, 130.0, 128.92, 128.86, 128.1, 127.7, 127.2, 126.9, 126.7, 126.4, 126.3, 122.6, 120.5, 54.0, 32.1, 21.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_3SNa^+$ 478.1447; Found 478.1457.



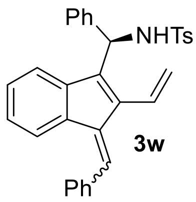
**3u**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-1-phenylprop-2-en-1-one **1k** (25.8 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3u**: 30.7 mg (0.0593 mmol), as a yellow solid, 59% yield; mp = 70–72 ℃; $[\alpha]_D^{25}$ = +86.7 (*c* = 0.27 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.98 min (minor), $t_R$ = 11.78 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09–7.99 (m, 2H), 7.78 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.66–7.59 (m, 1H), 7.57–7.49 (m, 2H), 7.49–7.40 (m, 4H), 7.36–7.27 (m, 3H), 7.10 (s, 1H), 7.08–6.98 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.83–6.77 (m, 1H), 6.46 (dd, *J* = 17.8, 11.5 Hz, 1H), 5.97 (d, *J* = 8.8 Hz, 1H), 5.53 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.45 (d, *J* = 8.8 Hz, 1H), 5.29 (dd, *J* = 17.8, 1.6 Hz, 1H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.0, 147.1, 143.5, 141.4, 140.5, 138.2, 137.9, 137.4, 136.6, 133.8, 133.5, 129.5, 129.0, 128.90, 128.87, 128.1, 127.8, 126.9, 126.8, 126.7, 125.7, 125.5, 122.7, 120.5, 54.0, 21.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NO_3SNa^+$ 544.1604; Found 544.1606.



**3v**

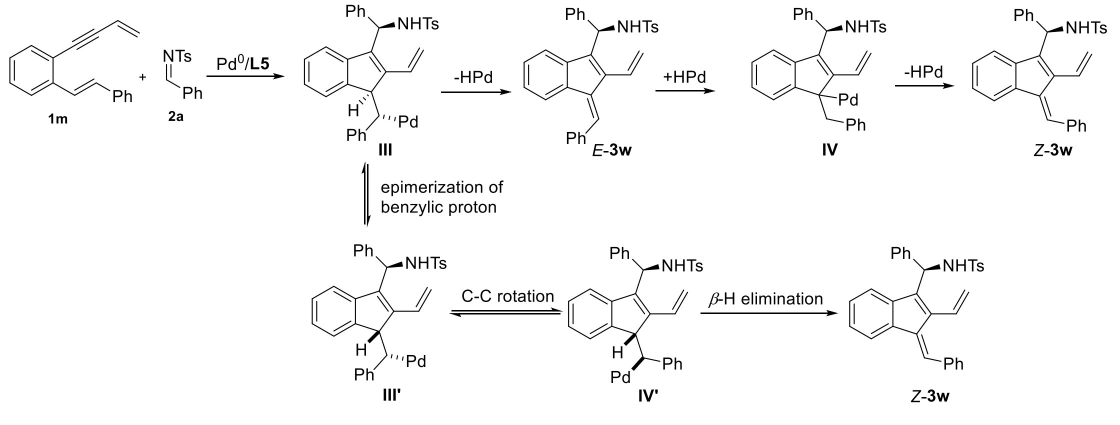
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-*N*,*N*-dimethylacrylamide **1l** (22.5 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 ℃ for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3v**: 37.2 mg (0.0767 mmol), as a yellow solid, 77% yield; mp = 226–228 ℃; $[\alpha]_D^{25}$ = +98.0 (*c* = 0.26 in $CHCl_3$); 85% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.28 min (minor), $t_R$ = 6.57 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55–7.35 (m, 5H), 7.33–7.26 (m, 3H), 7.12–6.92 (m, 4H), 6.88–6.79 (m, 1H), 6.52 (s, 1H), 6.39 (dd, *J* = 17.8, 11.5 Hz, 1H), 5.92 (d, *J* = 8.5 Hz, 1H), 5.45 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.38 (d, *J* = 8.5 Hz, 1H), 5.24 (dd, *J* = 17.8, 1.7 Hz, 1H), 3.14 (s, 3H), 3.02 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.4, 143.4, 141.7, 140.9, 138.7, 138.4, 136.74, 136.67, 133.7, 129.1, 128.8, 128.7, 127.9, 127.8, 127.0, 126.7, 126.3, 123.30, 123.26, 122.2, 120.4, 53.9, 37.7, 34.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{28}N_2O_3SNa^+$ 507.1713; Found 507.1723.



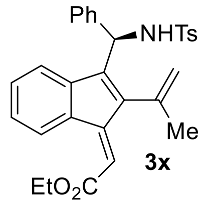
**3w**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added 1-(but-3-en-1-yn-1-yl)-2-styrylbenzene **1m** (23.0 mg, 0.0999 mmol, 1.0 equiv, *E*/*Z* = 2.7:1), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3w**: 34.7 mg (0.0714 mmol), as a yellow solid, 71% yield; mp = 61–63 °C; $[\alpha]_D^{25}$ = +142.4 (*c* = 0.55 in $CHCl_3$); *E/Z* = 2.5:1, 84% ee/89% ee, determined by HPLC analysis [Daicel Chiralpak IF, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.96 min (major), $t_R$ = 8.11 min (minor); $t_R$ = 7.63 min (minor), $t_R$ = 9.51 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55–7.38 (m, 9H), 7.36–7.26 (m, 7H), 7.22 (s, 1H), 7.04–6.94 (m, 3H), 6.92–6.81 (m, 3H), 6.48 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.04–5.94 (m, 1H), 5.55–5.40 (m, 2H), 5.23 (dd, *J* = 17.8, 1.8 Hz, 1H), 5.05–4.90 (m, 1H), 2.25 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 142.9, 141.1, 139.5, 138.9, 138.6, 136.9, 136.5, 136.2, 134.5, 133.3, 130.6, 129.2, 128.9, 128.7, 128.5, 127.8, 127.0, 126.9, 125.2, 123.1, 121.7, 120.1, 54.1, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}NO_2SNa^+$ 512.1655; Found 512.1662.

## Propose process for the formation of Z-3w

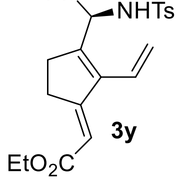


Reaction of 2-styrylbenzene substituted enyne **1m** with N-Ts imine **2a** under the standard conditions would deliver $\eta^1$-benzyl-Pd(II) intermediate **III** after vinylogous addition and 5-*exo-trig* migratory insertion, which underwent β-H elimination to form ***E*-3w**. As demonstrated in a previous study (*Tetrahedron Lett.*, 2013, **54**, 5808), ***E*-3w** would feasibly undergo reversible hydropalladation and β-H elimination to form ***Z*-3w**. A base-mediated epimerization at the benzylic position of the intermediate **III** also might be possible for the formation of ***Z*-3w** isomer.



**3x**

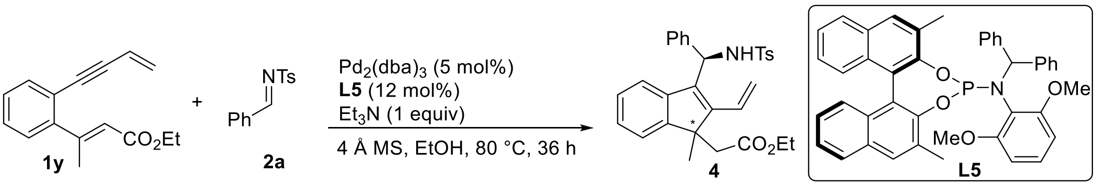
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(3-methylbut-3-en-1-yn-1-yl)phenyl)acrylate **1n** (24.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3x**: 38.9 mg (0.0778 mmol), as a yellow solid, 78% yield; mp = 51−53 °C; $[\alpha]^{25}_{D}$ = +61.0 (*c* = 0.32 in CHCl$_3$); 91% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.38 min (minor), $t_R$ = 6.81 min (major); $^1$H NMR (400 MHz, CDCl3) δ (ppm) 8.46 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.61–7.50 (m, 2H), 7.38–7.30 (m, 2H), 7.29–7.20 (m, 3H), 7.17–6.97 (m, 4H), 6.86 (d, *J* = 7.2, 1H), 6.19 (s, 1H), 5.79 (d, *J* = 7.9 Hz, 1H), 5.43 (d, *J* = 7.8 Hz, 1H), 5.37–5.28 (m, 1H), 4.78 (dd, *J* = 2.1, 1.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.83 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 166.1, 150.1, 143.4, 143.3, 141.8, 139.8, 138.5, 137.8, 137.1, 132.9, 129.7, 129.1, 128.7, 127.9, 127.2, 127.0, 126.9, 126.6, 120.6, 119.54, 119.48, 60.9, 54.5, 24.5, 21.4, 14.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710; Found 522.1716.



**3y**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-nona-2,8-dien-6-ynoate **1o** (17.8 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), Pd$_2$(dba)$_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%), BzOH (2.5 mg, 20 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then Et$_3$N (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **3y**: 26.1 mg (0.0597 mmol), as a white semisolid, 60% yield; $[\alpha]_D^{25}$ = +84.6 (*c* = 0.35 in $CHCl_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak IF, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.38 min (major), $t_R$ = 7.15 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71–7.61 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.17 (m, 5H), 6.25–6.18 (m, 1H), 5.73 (t, *J* = 2.5 Hz, 1H), 5.65 (d, *J* = 8.1 Hz, 1H), 5.46 (dd, *J* = 11.6, 1.6 Hz, 1H), 5.33 (dd, *J* = 8.2, 2.9 Hz, 1H), 5.27 (dd, *J* = 17.9, 1.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.93–2.79 (m, 1H), 2.71–2.58 (m, 1H), 2.36 (s, 3H), 2.33–2.22 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 166.2, 153.2, 143.7, 140.3, 138.1, 137.1, 129.4, 128.9, 128.03, 128.00, 127.1, 126.5, 121.7, 108.8, 59.6, 55.7, 30.3, 29.2, 21.4, 14.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{27}NO_4SNa^+$ 460.1553; Found 460.1563.

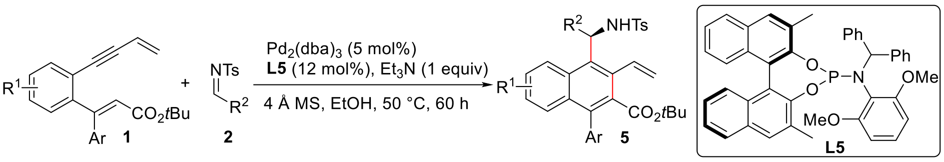
## 5. General procedure for asymmetric synthesis of indene derivative 4



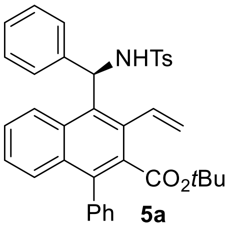
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)but-2-enoate **1y** (24.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 80 °C for 36 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **4**: 30.1 mg (0.0598 mmol), as a colourless oil, 60% yield; 2.2:1 dr, determined by $^1$H NMR; 87% ee/70% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.99 min (major), $t_R$ = 8.97 min (minor); $t_R$ = 10.23 min (minor), $t_R$ = 11.37 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61–7.56 (m, 2H), 7.53–7.46 (m, 2H), 7.32–7.28 (m, 3H), 7.17–7.05 (m, 5H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.30 (dd, *J* = 17.8, 11.6 Hz, 1H), 5.90 (d, *J* = 8.3 Hz, 1H), 5.36 (d, *J* =

8.3 Hz, 1H), 5.33–5.26 (m, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 2.84 (d, *J* = 14.2 Hz, 1H), 2.67 (d, *J* = 14.2 Hz, 1H), 2.33 (s, 3H), 1.13 (s, 3H), 0.82 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.9, 151.3, 148.1, 143.3, 139.6, 139.2, 137.4, 136.4, 129.5, 128.5, 128.0, 127.5, 127.3, 127.0, 126.8, 126.7, 125.9, 122.1, 120.9, 118.5, 60.0, 53.0, 51.2, 42.2, 24.2, 21.4, 13.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{31}NO_4SNa^+$ 524.1866; Found 524.1868.

## 6. General procedure for asymmetric synthesis of naphthalenes 5



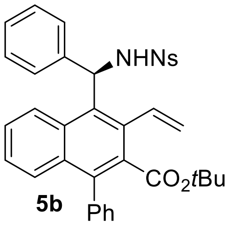
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added 1,3-enyne derivative **1** (0.100 mmol), imine **2** (0.200 mmol), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 48−60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give product **5**.



**5a**

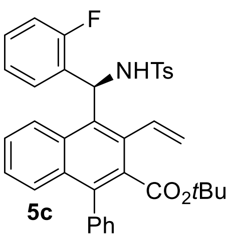
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **2a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5a**: 47.6 mg (0.0807 mmol), as a white solid, 81% yield; mp =137−139 °C; $[\alpha]_D^{25}$ = +109.8 (*c* = 0.51 in $CHCl_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 10.81 min (major), $t_R$ = 12.59 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55–7.36 (m, 7H), 7.36–7.26 (m, 7H), 7.25–7.20 (m, 2H), 6.98–6.80 (m, 2H), 6.80–6.67 (m, 1H), 6.64 (d, *J* = 9.6

Hz, 1H), 5.91 (s, 1H), 5.45 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.33 (dd, *J* = 17.9, 1.7 Hz, 1H), 2.27 (s, 3H), 1.16 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.5, 142.6, 140.5, 137.4, 137.2, 137.0, 134.1, 130.7, 130.4, 128.8, 128.7, 128.0, 127.9, 127.8, 127.5, 127.1, 126.6, 126.4, 125.9, 124.6, 122.2, 81.8, 27.6, 21.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{37}H_{35}NO_4SNa^+$ 612.2179; Found 612.2170.



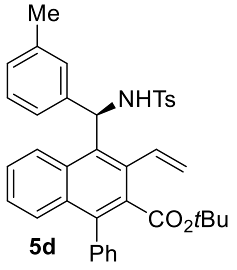
**5b**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-N-benzylidene-4-nitrobenzenesulfonamide **2o** (58.1 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5b**: 40.1 mg (0.0647 mmol), as a white solid, 65% yield; mp = 145−147 °C; $[\alpha]^{25}_{D}$ = +120.3 (*c* = 0.48 in $CHCl_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.96 min (major), $t_R$ = 9.59 min (minor); $^1$H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.86–7.78 (d, *J* = 8.3 Hz, 2H), 7.55–7.26 (m, 14H), 7.23–7.14 (m, 2H), 6.96–6.68 (m, 2H), 6.16 (brs, 1H), 5.52 (d, *J* = 11.6 Hz, 1H), 5.36 (d, *J* = 17.8 Hz, 1H), 1.16 (s, 9H); $^{13}$C NMR (150MHz, $CDCl_3$) δ (ppm) 167.2, 149.1, 145.4, 139.2, 137.7, 136.6, 130.5, 130.0, 128.9, 128.6, 128.3, 128.2, 128.13, 128.09, 128.0, 127.94, 127.89, 127.7, 127.3, 126.5, 126.2, 123.0, 122.9, 122.7, 82.2, 27.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{36}H_{32}N_2O_6SNa^+$ 643.1873; Found 643.1875.



**5c**

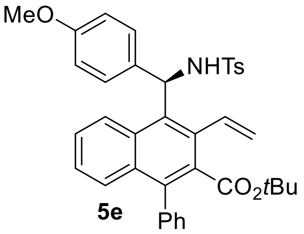
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv, ), (*E*)-*N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide **2l** (55.4 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5c**: 49.8 mg (0.0819 mmol), as a white solid, 82% yield; mp = 187−189 °C; $[\alpha]_D^{25}$ = +24.0 (*c* = 0.38 in $CHCl_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 14.00 min (major), $t_R$ = 19.90 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 8.5 Hz, 1H), 7.54–7.48 (m, 1H), 7.47–7.38 (m, 4H), 7.37–7.26 (m, 6H), 7.25–7.22 (m, 1H), 7.11–7.04 (m, 1H), 7.02–6.95 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.86–6.75 (m, 2H), 5.72 (d, *J* = 6.8 Hz, 1H), 5.43 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.26 (dd, *J* = 17.9, 1.7 Hz, 1H), 2.28 (s, 3H), 1.14 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 160.4(d, $^1J_{FC}$ = 247.3 Hz), 142.8, 137.5, 136.9, 134.4, 133.5, 133.3, 132.1, 131.2, 130.7, 130.4, 130.3, 129.7 (d, $^3J_{FC}$ = 3.1 Hz), 129.6, 129.5, 128.9, 127.9, 127.81 (d, $^2J_{FC}$ = 24.5 Hz), 127.77, 126.9, 126.8, 125.8, 124.6, 123.8 (d, $^3J_{FC}$ = 3.5 Hz), 122.2, 116.1 (d, $^2J_{FC}$ = 21.6 Hz), 81.7, 53.0, 27.6, 21.5; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) −111.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{34}FNO_4SNa^+$ 630.2085; Found 630.2088.



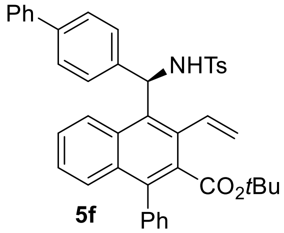
**5d**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide **2c** (54.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5d**: 47.2 mg (0.0782 mmol), as a white solid, 78% yield; mp = 99−101 °C; $[\alpha]_D^{25}$ = +40.8 (*c* = 0.26 in $CHCl_3$); 81% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.69 min (major), $t_R$ = 11.06 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44–7.33 (m, 4H), 7.36–7.25 (m, 5H), 7.25–7.03 (m, 6H), 6.91–6.81 (m, 2H), 6.81–6.68 (m, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 5.91 (brs, 1H), 5.46 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.35 (dd, *J* = 17.9, 1.7 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 1.17 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.6, 142.5, 140.4, 138.5, 137.4, 137.1, 137.0, 130.7, 130.4, 128.8, 128.5, 128.3, 128.0, 127.9, 127.8, 127.1, 126.4, 125.8, 123.7, 122.1, 81.8, 27.6, 21.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{37}NO_4SNa^+$ 626.2336;

Found 626.2337.

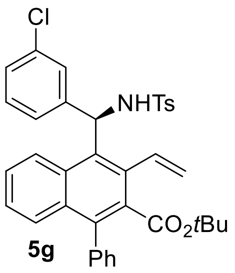

**5e**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(4-methoxybenzylidene)-4-methylbenzenesulfonamide **2m** (57.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **5e**: 38.7 mg (0.0623 mmol), as a white solid, 62% yield; mp = 168–170 °C; $[\alpha]_{\mathrm{D}}^{25}$ = +33.8 (*c* = 0.49 in $CHCl_3$); 71% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 15.26 min (major), $t_R$ = 20.75 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67–7.38 (m, 5H), 7.38–7.26 (m, 6H), 7.24–7.17 (m, 2H), 6.94–6.79 (m, 4H), 6.79–6.64 (m, 1H), 6.64–6.43 (m, 1H), 5.84 (brs, 1H), 5.44 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.31 (d, *J* = 17.9 Hz, 1H), 3.78 (s, 3H), 2.27 (s, 3H), 1.16 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.5, 158.9, 142.5, 137.4, 137.1, 136.9, 132.3, 130.7, 130.39, 130.36, 128.8, 127.93, 127.87, 127.8, 127.0, 126.4, 125.8, 122.0, 114.0, 81.7, 55.3, 27.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{37}NO_5SNa^+$ 642.2285; Found 642.2285.


**5f**

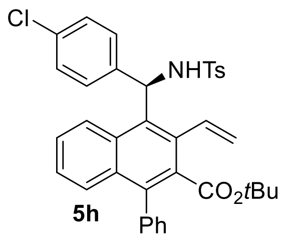
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-([1,1'-biphenyl]-4-ylmethylene)-4-methylbenzenesulfonamide **2e** (67.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5f**: 55.2 mg (0.0829 mmol), as a white solid, 83% yield; mp = 118–120 °C; $[\alpha]_{\mathrm{D}}^{25}$ = +50.0

($c$ = 0.54 in $CHCl_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 15.23 min (major), $t_R$ = 19.23 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52– 7.45 (m, 4H), 7.44–7.31 (m, 8H), 7.30–7.10 (m, 8H), 6.81 (s, 2H), 6.75–6.55 (m, 2H), 5.89 (brs, 1H), 5.40 (dd, $J$ = 11.5, 1.6 Hz, 1H), 5.329 (d, $J$ = 17.9 Hz, 1H), 2.20 (s, 3H), 1.09 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.5, 142.7, 140.5, 140.3, 137.4, 137.3, 137.0, 130.7, 130.4, 128.9, 128.8, 128.0, 127.93, 127.86, 127.42, 127.36, 127.1, 126.5, 81.8, 27.6, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{43}H_{39}NO_4SNa^+$ 688.2492; Found 688.2496.



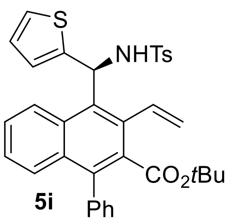
**5g**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(3-chlorobenzylidene)-4-methylbenzenesulfonamide **2g** (58.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5g**: 46.7 mg (0.0748 mmol), as a white solid, 75% yield; mp = 164–166 °C; $[\alpha]_D^{25}$ = +63.7 ($c$ = 0.63 in $CHCl_3$); 83% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.19 min (major), $t_R$ = 10.40 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43–7.33 (m, 5H), 7.30–24 (m, 2H), 7.24–7.11 (m, 8H), 6.93–6.73 (m, 2H), 6.69–6.55 (m, 1H), 6.55–6.40 (m, 1H), 5.84 (brs, 1H), 5.39 (dd, $J$ = 11.4, 1.5 Hz, 1H), 5.26 (dd, $J$ = 17.8, 1.5 Hz, 1H), 2.22 (s, 3H), 1.09 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.4, 142.9, 137.5, 137.3, 136.8, 134.8, 130.7, 130.3, 129.9, 129.0, 128.0, 127.93, 127.90, 127.7, 127.4, 126.6, 126.4, 126.0, 124.9, 81.9, 27.6, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{34}{}^{35}ClNO_4SNa^+$ 646.1789; Found 646.1790; Calcd for $C_{37}H_{34}{}^{37}ClNO_4SNa^+$ 647.1823; Found 647.1816.



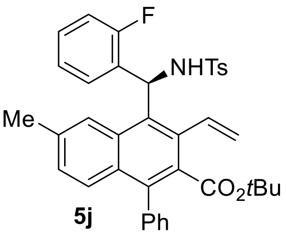
**5h**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **2h** (58.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5h**: 50.0 mg (0.0801 mmol), as a white solid, 80% yield; mp = 99–101 °C; $[\alpha]_D^{25}$ = +64.9 (*c* = 0.25 in $CHCl_3$); 81% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.23 min (major), $t_R$ = 11.48 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51–7.44 (m, 5H), 7.43–7.34 (m, 2H), 7.34–7.18 (m, 8H), 7.03–6.76 (m, 2H), 6.78–6.60 (m, 1H), 6.60–6.43 (m, 1H), 5.91 (brs, 1H), 5.45 (dd, *J* = 11.4, 1.5 Hz, 1H), 5.30 (d, *J* = 17.8 Hz, 1H), 2.29 (s, 3H), 1.16 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.4, 142.9, 137.5, 137.3, 136.8, 133.4, 130.7, 130.3, 128.9, 128.8, 128.1, 128.0, 127.93, 127.90, 127.3, 126.5, 126.0, 81.9, 27.6, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{34}{}^{35}ClNO_4SNa^+$ 646.1789; Found 646.1795; Calcd for $C_{37}H_{34}{}^{37}ClNO_4SNa^+$ 647.1823; Found 647.1823.



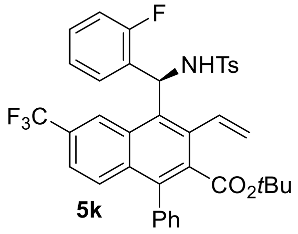
**5i**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide **2k** (53.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 μL, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5i**: 36.9 mg (0.0619 mmol), as a white solid, 62% yield; $[\alpha]_D^{25}$ = +40.8 (*c* = 0.51 in $CHCl_3$); 73% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 12.16 min (major), $t_R$ = 14.64 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06–7.55 (m, 1H), 7.54–7.39 (m 4H), 7.39–7.26 (m, 5H), 7.26–7.21 (m, 2H), 7.02–6.56 (m, 6H), 6.00 (brs, 1H), 5.51 (d, $J$ = 11.4 Hz, 1H), 5.40 (d, $J$ = 17.8 Hz, 1H), 2.27 (s, 3H), 1.17 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.4, 145.3, 142.8, 137.5, 137.3, 136.7, 130.7, 130.3, 128.8, 128.0, 127.90, 127.85, 127.2, 126.5, 125.9, 125.5, 125.4, 122.4, 81.8, 27.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{33}NO_4S_2Na^+$ 618.1743; Found 618.1736.

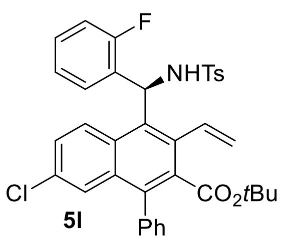


**5j**

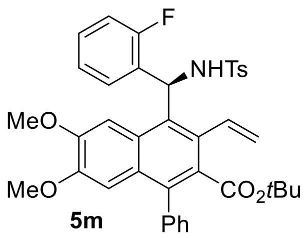
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)-3-phenylacrylate **1q** (34.4 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5j**: 45.7 mg (0.0734 mmol), as a white solid, 73% yield; mp = 125−127 °C; $[\alpha]_D^{25}$ = +19.6 ($c$ = 0.25 in $CHCl_3$); 89% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 12.03 min (major), $t_R$ = 21.50 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (s, 1H), 7.61–7.54 (m, 1H), 7.50–7.40 (m, 3H), 7.39–7.33 (m, 2H), 7.32–7.25 (m, 4H), 7.14–7.06 (m, 2H), 7.03–6.89 (m, 3H), 6.82–6.69 (m, 2H), 5.81–5.69 (m, 1H), 5.40 (dd, $J$ = 11.4, 1.7 Hz, 1H), 5.25 (dd, $J$ = 17.9, 1.7 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 1.13 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.7, 160.4 (d, $^1J_{FC}$ = 247.3 Hz), 142.8, 137.7, 137.4, 136.9, 136.7, 134.6, 133.4, 132.5, 130.7, 130.6, 130.4, 130.3, 129.7 (d, $^4J_{FC}$ = 3.1 Hz), 129.5 (d, $^3J_{FC}$ = 8.2 Hz), 128.9, 128.0, 127.81, 127.80 (d, $^2J_{FC}$ = 21.9 Hz), 127.5, 127.1, 127.0 (d, $^3J_{FC}$ = 11.9 Hz), 126.8, 123.8, 123.6, 122.0, 116.0 (d, $^2J_{FC}$ = 21.5 Hz), 115.9, 52.9, 27.6, 22.1, 21.5; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –112.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{36}FNO_4SNa^+$ 644.2234; Found 644.2234.


**5k**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl-3-(2-(but-3-en-1-yn-1-yl)-4-(trifluoromethyl)phenyl)-3-phenylacrylate **1r** (39.8 mg, 0.0999 mmol, 1.0 equiv, *E/Z* = 11:1), (*E*)-*N*-(2-fluorobenzy-lidene)-4-methylbenzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5k**: 43.8 mg (0.0648 mmol), as a white solid, 65% yield; mp = 62–64 °C; $[\alpha]_D^{25}$ = +9.4 (*c* = 0.43 in $CHCl_3$); 87% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.38 min (major), $t_R$ = 9.85 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (s, 1H), 7.44–7.30 (m, 6H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.25–7.18 (m, 3H), 7.05–6.99 (m, 1H), 6.99–6.90 (m, 1H), 6.87–6.75 (m, 3H), 6.72 (d, *J* = 5.8 Hz, 1H), 5.56 (d, *J* = 5.8 Hz, 1H), 5.43 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.27 (dd, *J* = 17.9, 1.6 Hz, 1H), 2.15 (s, 3H), 1.08 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.0, 160.2 (d, $^1J_{FC}$ = 246.6 Hz), 142.9, 137.6, 136.7, 136.5, 135.4, 135.2, 133.9, 133.4, 132.2, 130.6, 130.2, 130.0, 129.9 (d, $^3J_{FC}$ = 8.3 Hz), 129.4 (d, $^3J_{FC}$ = 3.1 Hz), 129.0 (q, $^1J_{FC}$ = 252.1 Hz),128.8, 128.7 (d, $^2J_{FC}$ = 21.6 Hz), 128.23, 128.18, 128.1, 127.9, 126.9, 126.1 (d, $^2J_{FC}$ = 12.1 Hz), 125.4, 124.1, 122.73, 122.6 (q, $^3J_{FC}$ = 3.1 Hz), 121.3 (q, $^3J_{FC}$ = 3.2 Hz), 116.2 (d, $^2J_{FC}$ = 21.5 Hz), 82.3, 52.8, 27.6, 21.4; $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –112.4, –62.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{38}H_{33}F_4NO_4SNa^+$ 698.1959; Found 698.1957.

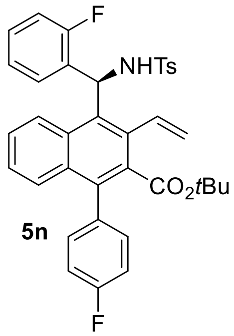

**5l**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-5-chlorophenyl)-3-phenylacrylate **1s** (36.4 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5l**: 46.3 mg (0.0721 mmol), as a white solid, 72% yield; mp = 174–176 °C; $[\alpha]_D^{25}$ = +23.2 (*c* = 0.41 in $CHCl_3$); 83% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.34 min (major), $t_R$ = 10.37 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 9.2 Hz, 1H), 7.53–7.38 (m, 4H), 7.38–7.32 (m, 3H), 7.31–7.26 (m, 3H), 7.26–7.23 (m, 1H), 7.11–6.98 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.85–6.69 (m, 2H), 5.67 (d, *J* = 6.5 Hz, 1H), 5.45 (dd, *J* = 11.5, 1.6 Hz, 1H), 5.27 (dd, *J* = 17.8, 1.7 Hz, 1H), 2.28 (s, 3H), 1.14 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 167.2, 160.4 (d, $^1J_{FC}$ = 247.3 Hz), 143.0, 136.8, 136.72, 136.70, 134.4, 134.0, 133.9, 133.1, 132.1, 131.4, 130.6, 130.3, 129.9, 129.8 (d, $^3J_{FC}$ = 8.2 Hz), 129.7 (d, $^3J_{FC}$ = 3.1 Hz), 128.9, 128.8, 128.2, 128.12, 128.10, 127.5, 126.8, 126.6, 126.4 (d, $^2J_{FC}$ = 11.9 Hz), 126.1, 124.0, 122.4, 116.2 (d, $^2J_{FC}$ = 21.5 Hz), 52.9, 27.6, 21.5. $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –112.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{33}{}^{35}ClFNO_4SNa^+$ 664.1695; Found 664.1698; Calcd for $C_{37}H_{33}{}^{37}ClFNO_4SNa^+$ 665.1729; Found 665.1728.



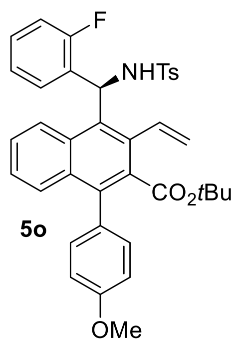
**5m**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl-3-(2-(but-3-en-1-yn-1-yl)-4,5-dimethoxyphenyl)-3-phenyl acrylate **1t** (39.0 mg, 0.0999 mmol, 1.0 equiv, *E*/*Z* = 2.5:1), (*E*)-*N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **5m**: 56.0 mg (0.0844 mmol), as a white solid, 84% yield; mp = 213–215 °C; $[\alpha]_D^{25}$ = +108.8 (*c* = 0.68 in $CHCl_3$); 85% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 9.75 min (major), $t_R$ = 20.01 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83–7.69 (m, 2H), 7.48–7.41 (m, 4H), 7.36–7.28 (m, 2H), 7.26–7.20 (m, 2H), 7.13–7.09 (m, 1H), 7.07–7.00 (m, 2H), 6.98–6.92 (m, 1H), 6.69–6.66 (m, 1H), 6.61 (s, 1H), 5.94–5.76 (m, 1H), 5.34 (dd, *J* = 11.3, 1.8 Hz, 1H), 5.21 (dd, *J* = 17.9, 1.9 Hz, 1H), 5.05 (s, 1H), 3.78 (s, 3H), 3.57 (s, 3H), 2.32 (s, 3H), 1.13 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 168.0, 161.5 (d, $^{1}J_{FC}$ = 247.3 Hz), 149.6, 148.9, 143.4, 143.1, 137.0, 136.1, 134.5, 132.0, 131.9, 130.5, 130.1, 130.0 (d, $^{2}J_{FC}$ = 20.3 Hz), 129.7, 129.5, 129.4 (d, $^{3}J_{FC}$ = 8.2 Hz), 129.1, 128.1, 128.0, 127.7, 127.4 (d, $^{3}J_{FC}$ = 11.9 Hz), 127.0, 126.4, 126.3, 123.7, 121.7, 116.1 (d, $^{2}J_{FC}$ = 21.5 Hz), 106.0, 104.1, 81.5, 56.0, 55.4, 53.3, 27.6, 21.5; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –112.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{39}H_{38}FNO_6SNa^+$ 690.2296; Found 690.2293.



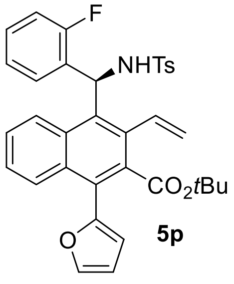
**5n**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(4-fluorophenyl)-acrylate **1u** (34.8 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 *μ*L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5n**: 39.2 mg (0.0627 mmol), as a white solid, 63% yield; mp = 176–178 °C; $[\alpha]_D^{25}$ = +30.3 (*c* = 0.37 in $CHCl_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.87 min (major), $t_R$ = 8.29 min (minor); $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04–7.93 (m, 1H), 7.55–7.47 (m, 1H), 7.42–7.32 (m, 4H), 7.32–7.26 (m, 3H), 7.25–7.21 (m, 1H), 7.20–7.12 (m, 2H), 7.11–7.04 (m, 1H), 7.02–6.95 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.83–6.72 (m, 2H), 5.68 (d, *J* = 7.2 Hz, 1H), 5.43 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.26 (dd, *J* = 17.8, 1.7 Hz, 1H), 2.28 (s, 3H), 1.18 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 167.5, 162.3 (d, $^{1}J_{FC}$ = 325.9 Hz), 160.6 (d, $^{1}J_{FC}$ = 327.6 Hz), 142.8, 136.9, 136.3, 134.2, 133.6, 133.4, 133.3, 132.4 (d, $^{3}J_{FC}$ = 8.5 Hz), 132.14, 132.06, 132.0, 131.6, 130.3, 129.6, 129.62, 129.60, 129.5, 128.9, 127.4, 126.9, 126.83, 126.76, 125.9, 124.7, 123.8 (d, $^{3}J_{FC}$ = 3.6 Hz), 122.3, 116.1 (d, $^{2}J_{FC}$ = 21.5 Hz), 115.0 (d, $^{3}J_{FC}$ = 4.5 Hz), 114.8 (d, $^{3}J_{FC}$ = 4.4 Hz), 81.9, 53.0, 27.6, 21.5; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –114.2, –112.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{37}H_{33}F_2NO_4SNa^+$ 648.1991; Found 648.1994.



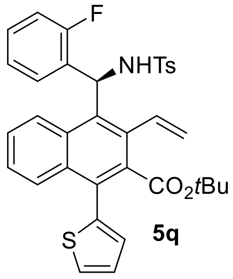
**5o**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(4-methoxyphenyl)-acrylate **1v** (36.0 mg, 0.0999 mmol, 1.0 equiv, *E/Z* = 3.1:1), (*E*)-*N*-(2-fluorobenzylidene)-4-methyl-benzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **5o**: 48.3 mg (0.0757 mmol), as a white solid, 76% yield; mp = 177–179 °C; $[\alpha]_D^{25}$ = +27.4 (*c* = 0.38 in $CHCl_3$); 86% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.23 min (major), $t_R$ = 10.40 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, *J* = 8.5 Hz, 1H), 7.55–7.47 (m, 1H), 7.46–7.41 (m, 1H), 7.38–7.30 (m, 3H), 7.30–7.26 (m, 1H), 7.25–7.17 (m, 3H), 7.11–7.04 (m, 1H), 7.03–6.95 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.85–6.74 (m, 2H), 5.70 (d, *J* = 7.2 Hz, 1H), 5.43 (dd, *J* = 11.4, 1.7 Hz, 1H), 5.25 (dd, *J* = 17.8, 1.7 Hz, 1H), 3.88 (s, 3H), 2.27 (s, 3H), 1.19 (s, 9H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 167.7, 160.4 (d, $^1J_{FC}$ = 247.8 Hz), 159.3, 142.7, 137.2, 136.9, 134.3, 133.6, 133.5, 132.5, 131.8, 131.5, 131.0, 130.3, 129.7 (d, $^3J_{FC}$ = 3.0 Hz), 129.6, 129.5, 128.8, 126.9(d, $^2J_{FC}$ = 12.0 Hz), 126.8, 126.7, 125.7, 124.6, 123.8, 122.1, 116.1 (d, $^2J_{FC}$ = 21.5 Hz), 113.4, 113.3, 81.7, 55.4, 53.0, 27.7, 21.5; $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –111.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{36}FNO_5SNa^+$ 660.2190; Found 660.2188.



**5p**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(furan-2-yl)acrylate **1w** (32.0 mg, 0.0999 mmol, 1.0 equiv, *E/Z* = 3.1:1), (*E*)-*N*-(2-fluorobenzylidene)-4-methyl-benzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 48 h, and monitored by TLC. After completion, the solvent was evaporated *in* *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5p**: 41.5 mg (0.0695 mmol), as a white solid, 70% yield; mp = 104–106 °C; $[\alpha]^{25}_{D}$ = +14.4 (*c* = 0.20 in $CHCl_3$); 88% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.63 min (major), $t_R$ = 9.09 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97–7.86 (m, 1H), 7.70–7.57 (m, 2H), 7.49–7.31 (m, 3H), 7.30–7.26 (m, 1H), 7.24–7.18 (m, 2H), 7.10–6.95 (m, 2H), 6.90–6.70 (m, 4H), 6.62–6.47 (m, 2H), 5.66 (d, *J* = 7.2 Hz, 1H), 5.45 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.23 (dd, *J* = 17.8, 1.7 Hz, 1H), 2.22 (s, 3H), 1.38 (s, 9H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 167.3, 160.4 (d, $^1J_{FC}$ = 247.3 Hz), 149.4, 142.9, 142.8, 136.4, 134.7, 134.0, 132.2, 130.4, 129.8, 129.7, 129.7, 128.7, 127.1, 127.0, 126.8, 126.5 (d, $^3J_{FC}$ = 8.2 Hz), 126.4, 126.3, 124.8, 123.9 (d, $^3J_{FC}$ = 3.5 Hz), 122.4, 116.2 (d, $^2J_{FC}$ = 21.8 Hz), 112.0, 111.0, 82.1, 53.3, 27.9, 21.3; $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –111.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{32}FNO_5SNa^+$ 620.1887; Found 620.1883.

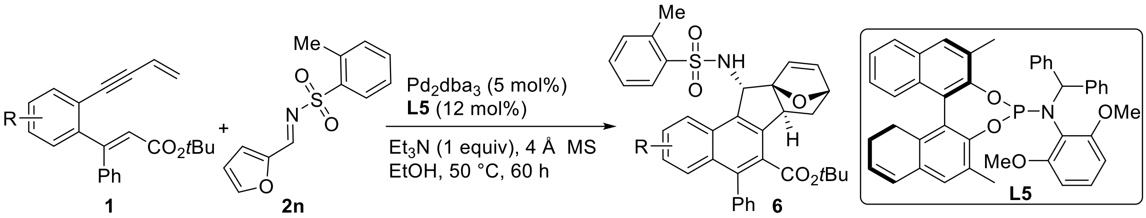


5q

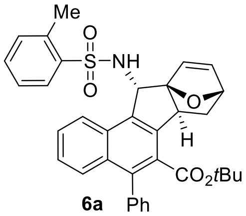
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*Z*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-(thiophen-2-yl)acrylate **1x** (33.6 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide **2l** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 48 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 5/1) to give product **5q**: 51.2 mg (0.0835 mmol), as a white solid, 84% yield; mp = 107–109 °C; $[\alpha]^{25}_{D}$ = +15.2 (*c* = 0.33 in $CHCl_3$); 87% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.36 min (major), $t_R$ = 9.34 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00–7.89 (m, 1H), 7.65–7.56 (m, 1H), 7.53–7.48 (m, 1H), 7.48–7.41 (m, 1H), 7.38–7.25 (m, 5H), 7.17–7.11 (m, 1H), 7.11–6.96 (m, 3H), 6.92–6.72 (m, 4H), 5.70 (d, *J* = 7.1 Hz, 1H), 5.46 (dd, *J* = 11.4, 1.7 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.7 Hz, 1H), 2.27 (s, 3H), 1.25 (s, 9H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 167.2, 160.4 (d, $^1J_{FC}$ = 247.3 Hz), 142.8, 137.1, 136.6, 135.2, 134.0, 133.1, 130.2, 129.9, 129.7 (d, $^3J_{FC}$ = 8.1 Hz), 128.7, 127.3, 126.9, 126.74, 126.73, 126.6, 126.5

(d, ${}^3J_{FC}$ = 7.8 Hz), 126.1, 124.6, 123.9, 122.5, 116.1 (d, ${}^2J_{FC}$ = 21.5 Hz), 82.0, 53.1, 27.7, 21.6; ${}^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –111.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{32}FNO_4S_2Na^+$ 636.1649; Found 636.1643.

## 7. General procedure for catalytic cascade reaction



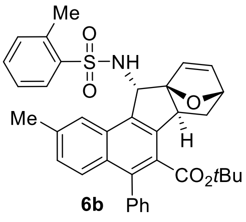
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added β-aryl-acrylate derived 1,3-enyne **1** (0.100 mmol), 2-furfural derived imine **2n** (49.8 mg, 0.200 mmol, 0.200 mmol), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give product **6**.



**6a**

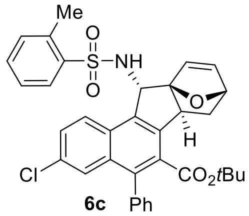
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-2-methylbenzene-sulfonamide **2n** (49.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 4/1 to 5/1) to give product **6a**: 39.3 mg (0.0679 mmol), as a white solid, 68% yield, >19:1 dr, determined by ${}^1$H NMR; mp = 119–121 °C; $[\alpha]_D^{25}$ = –68.3 (*c* = 0.36 in $CHCl_3$); 75% ee, determined by HPLC analysis [Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.08 min (minor), $t_R$ = 10.33 min (major); ${}^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58–7.54 (m, 1H), 7.51–7.39 (m, 5H), 7.38–7.27 (m, 3H), 7.23–

7.15 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 6.0 Hz, 1H), 6.33 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.34 (d, *J* = 7.5 Hz, 1H), 5.08 (dd, *J* = 4.5, 1.7 Hz, 1H), 5.05–4.97 (m, 1H), 3.70 (dd, *J* = 8.4, 3.8 Hz, 1H), 2.51 (s, 3H), 2.01–1.94 (m, 1H), 1.83–1.76 (m, 1H), 1.14 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.8, 141.7, 140.3, 138.3, 138.2, 137.4, 136.1, 134.7, 134.0, 133.1, 132.6, 132.3, 130.9, 130.4, 130.1, 129.5, 128.3, 128.0, 127.7, 127.6, 127.62, 126.59, 126.1, 123.1, 98.0, 81.9, 80.6, 56.5, 49.2, 30.8, 27.5, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{33}NO_5SNa^+$ 602.1972; Found 602.1981.



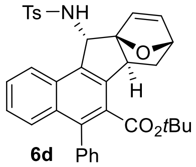
**6b**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)-3-phenylacrylate **1q** (34.4 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-2-methylbenzenesulfonamide **2n** (49.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **6b**: 42.8 mg (0.0722 mmol), as a white solid, 72% yield, >19:1 dr, determined by $^1$H NMR; mp = 133−135 °C; $[\alpha]_D^{25} = -79.7$ (*c* = 0.71 in $CHCl_3$); 76% ee, determined by HPLC analysis [Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.98 min (minor), $t_R$ = 7.34 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55–7.50 (m, 1H), 7.49–7.36 (m, 5H), 7.35–7.31 (m, 2H), 7.23–7.17 (m, 1H), 7.11 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.98 (s, 1H), 6.70 (d, *J* = 6.0 Hz, 1H), 6.33 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.35 (d, *J* = 7.6 Hz, 1H), 5.07 (dd, *J* = 4.5, 1.7 Hz, 1H), 5.00 (d, *J* = 7.6 Hz, 1H), 3.71 (dd, *J* = 8.4, 3.8 Hz, 1H), 2.54 (s, 3H), 2.20 (s, 3H), 2.00–1.92 (m, 1H), 1.79 (dd, *J* = 11.5, 8.4 Hz, 1H), 1.15 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 141.9, 140.2, 138.5, 137.7, 137.1, 135.3, 134.5, 134.2, 133.1, 132.7, 130.9, 130.5, 130.0, 129.5, 129.4, 128.34, 128.26, 127.8, 127.6, 127.5, 126.5, 122.1, 98.1, 81.7, 80.6, 56.6, 49.2, 30.9, 27.5, 21.8, 20.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{35}NO_5SNa^+$ 616.2128; Found 616.2124.



**6c**

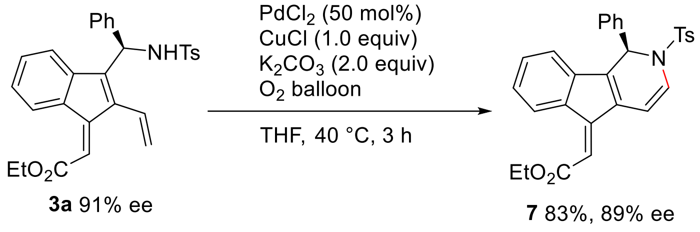
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)-5-chlorophenyl)-3-phenylacrylate **1s** (39.8 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-benzylidene-2-methylbenzenesulfonamide **2n** (49.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **6c**: 36.9 mg (0.0602 mmol), as a white solid, 60% yield, >19:1 dr, determined by $^1$H NMR; mp = 163–165 °C; $[\alpha]_D^{25} = -78.0$ ($c$ = 0.40 in $CHCl_3$); 75% ee, determined by HPLC analysis [Daicel Chiralpak IB, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 5.37 min (minor), $t_R$ = 6.59 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.60–7.53 (m, 1H), 7.52–7.28 (m, 7H), 7.19–7.15 (m, 1H), 7.13 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.58 (d, *J* = 5.9 Hz, 1H), 6.32 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.30 (d, *J* = 7.7 Hz, 1H), 5.11 (d, *J* = 7.8 Hz, 1H), 5.07 (dd, *J* = 4.4, 1.6 Hz, 1H), 3.67 (dd, *J* = 8.4, 3.8 Hz, 1H), 2.52 (s, 3H), 2.01–1.91 (m, 1H), 1.77 (dd, *J* = 11.5, 8.5 Hz, 1H), 1.14 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.4, 142.1, 139.4, 138.2, 137.5, 137.4, 136.4, 134.9, 133.7, 133.23, 133.19, 132.7, 132.2, 131.5, 130.8, 130.1, 129.4, 128.49, 128.45, 128.4, 128.0, 127.9, 126.74, 126.67, 124.8, 98.0, 82.2, 80.6, 56.4, 49.2, 30.7, 27.5, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{32}{}^{35}ClNO_5SNa^+$ 636.1582; Found 636.1591; Calcd for $C_{35}H_{32}{}^{37}ClNO_5SNa^+$ 637.1615; Found 637.1625.



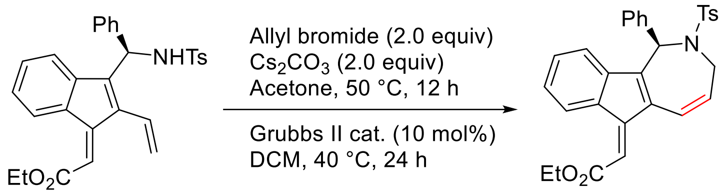
**6d**

To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar were added *tert*-butyl (*E*)-3-(2-(but-3-en-1-yn-1-yl)phenyl)-3-phenylacrylate **1p** (33.0 mg, 0.0999 mmol, 1.0 equiv), (*E*)-*N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide **2j** (49.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), **L5** (7.9 mg, 12 mol%) and 4 Å MS (60 mg). The tube was evacuated and back-filled with argon for three times. Then $Et_3N$ (14 $\mu$L, 0.10 mmol, 1.0 equiv) and degassed dry EtOH (1.0 mL) were added via syringe sequentially. The mixture was stirred at 50 °C for 60 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1 to 4/1) to give product **6d**: 42.7 mg (0.0742 mmol), 74% yield, 6:1 dr, determined by $^1$H NMR analysis; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, *J* = 8.0 Hz, 2H), 7.50–7.41 (m, 2H), 7.41–7.32 (m, 3H), 7.26 (s, 1H), 7.30–7.26 (m, 2H), 7.25–7.20 (m, 1H), 7.06–6.98 (m, 1H), 6.96–6.84 (m, 1H), 6.72–6.57 (m, 2H), 6.35 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.90–5.63 (m, 1H), 5.28 (d, *J* = 6.4 Hz, 1H), 5.07 (dd, *J* = 4.2, 1.7 Hz, 1H), 3.63 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.53 (s, 3H), 1.98–1.79 (m, 2H), 1.11 (s, 1H), 1.06 (s, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.5, 143.9, 142.2, 139.4, 137.5, 137.3, 136.3, 134.4, 134.1, 132.0, 130.6, 129.9, 129.5, 128.4, 128.3, 127.9, 127.8, 127.7, 126.7, 125.2, 98.1, 82.4, 80.6, 56.5, 49.6, 30.6, 27.3, 21.7.

## 8. Transformations of the products



To an oven-dried 10 mL tube equipped with a magnetic stir bar were added product **3a** (48.5 mg, 0.0999 mmol, 1.0 equiv), $PdCl_2$ (8.9 mg, 0.050 mmol, 0.5 equiv), CuCl (9.9 mg, 0.10 mmol, 1.0 equiv), and $K_2CO_3$ (27.6 mg, 0.200 mmol, 2.0 equiv). The tube was evacuated and back-filled three times with $O_2$. Then THF (1.0 mL) were added via syringe. The mixture was stirred at 40 °C for 3 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 6/1) to give product **7**: 40.2 mg (0.0832 mmol), as a brown thick oil, 83% yield; $[\alpha]_D^{25}$ = –65.5 (*c* = 0.60 in $CHCl_3$); 89% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 7.08 min (major), $t_R$ = 7.82 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57–8.50 (m, 1H), 7.52–7.47 (m, 2H), 7.44–7.38 (m, 2H), 7.24–7.19 (m, 3H), 7.17–7.06 (m, 4H), 6.91 (d, *J* = 7.0, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 4.0 Hz, 2H), 5.87 (d, *J* = 7.7 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 146.9, 143.9, 141.8, 138.7, 136.4, 135.8, 133.8, 130.3, 130.2, 129.6, 128.7, 128.6, 127.8, 127.5, 127.0, 126.6, 125.5, 118.5, 117.2, 102.1, 61.0, 57.3, 21.5, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{25}NO_4SNa^+$ 506.1397; Found 506.1393.

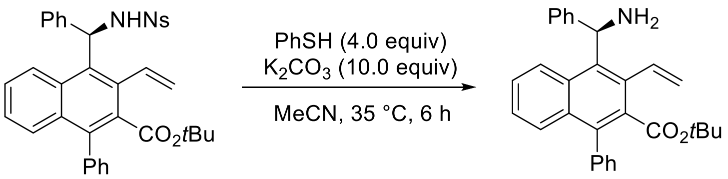


**3a** 91% ee

**8** 72%, 90% ee

To a solution of product **3a** (48.5 mg, 0.0999 mmol, 1.0 equiv) in acetone (1.0 mL) was added $Cs_2CO_3$ (65.0 mg, 0.200 mmol, 2.0 equiv). The resultant mixture was stirred at room temperature for 10 min, and allyl bromide (17.2 μL, 0.200 mmol, 2.0 equiv) was added slowly. After complete consumption of **3a** (monitored by TLC), the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether / EtOAc = 10/1) to give the *N*-allylation product.

To the solution of *N*-allylation product in DCM (1.0 mL) was added Hoveyda-Grubbs 2nd Generation Catalyst (6.3 mg, 0.010 mmol, 0.1 equiv). Then the mixture was degassed and charged with argon balloon and stirred at 40 °C for 24 h. After completion monitored by TLC, the mixture was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether = 7/1) to give product **8**: 35.8 mg (0.0720 mmol), as a yellow oil, 72% yield; $[\alpha]^{25}_{D}$ = +91.0 (*c* = 0.29 in $CHCl_3$); 90% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 6.06 min (major), $t_R$ = 6.99 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.53–8.43 (m, 1H), 7.50–7.43 (m, 2H), 7.36–7.27 (m, 5H), 7.23–7.16 (m, 2H), 7.02–6.94 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 6.10 (s, 1H), 5.99 (dd, *J* = 12.0, 2.9 Hz, 1H), 5.73–5.64 (m, 1H), 4.54–4.43 (m, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.64–3.52 (m, 1H), 2.24 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 149.4, 143.6, 143.5, 143.3, 137.3, 136.7, 133.2, 132.4, 130.5, 130.3, 129.1, 128.8, 128.62, 128.60, 127.5, 127.4, 126.9, 119.9, 119.0, 116.3, 61.0, 58.6, 44.7, 21.3, 14.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{27}NO_4SNa^+$ 520.1553; Found 520.1547.

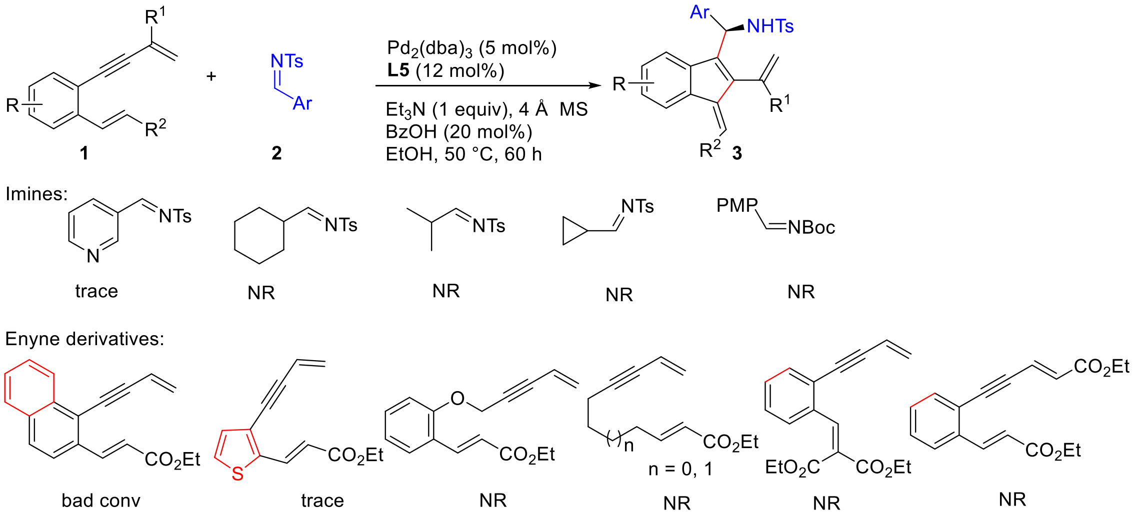


**5b** 82% ee

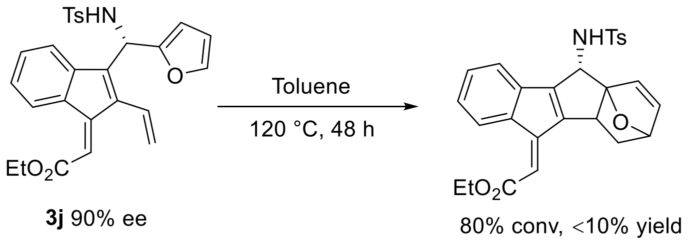
**9** 96%, 82% ee

To an oven-dried 10 mL tube equipped with a magnetic stir bar were added product **5b** (62.0 mg, 0.0999 mmol, 1.0 equiv), $K_2CO_3$ (138 mg, 1.00 mmol, 10.0 equiv). The tube was evacuated and back-filled with argon for three times. Then dry MeCN (1.0 mL) and PhSH (41 $\mu$L, 0.40 mmol, 4.0 equiv) were added via syringe sequentially. The mixture was stirred at 35 °C for 6 h, and monitored by TLC. After completion, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1 to 3/1) to give product **9**: 41.8 mg (0.0960 mmol), as a colourless oil, 96% yield; $[\alpha]_D^{25}$ = +143.0 (*c* = 0.59 in $CHCl_3$); 82% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm]: $t_R$ = 8.30 min (minor), $t_R$ = 12.74 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96–7.89 (m, 1H), 7.52–7.37 (m, 8H), 7.34–7.29 (m, 2H), 7.27–7.26 (m, 1H), 7.24–7.18 (m, 2H), 7.12 (dd, *J* = 17.3, 11.8 Hz, 1H), 6.11 (s, 1H), 5.55 (s, 1H), 5.54–5.49 (m, 1H), 2.08–1.99 (m, 2H), 1.18 (s, 9H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 168.2, 145.0, 138.4, 137.9, 136.6, 135.0, 133.2, 132.9, 132.7, 130.7, 130.6, 130.4, 128.3, 127.9, 127.7, 127.6, 126.3, 126.2, 126.0, 125.7, 121.3, 81.7, 54.4, 27.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{30}NO_2^+$ 436.2271; Found 436.2275.

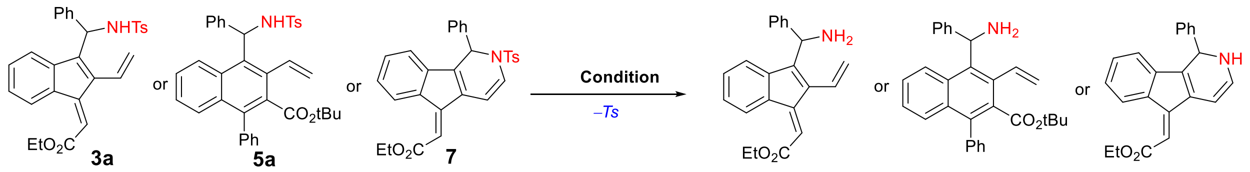
## 9. More substrates and transformation exploration



To further expand the substrate scope, several imines and alkene-tethered enynes were investigated under the optimal conditions. Unfortunately, these substrates generally showed low reactivity, and no apparent transformations were observed.



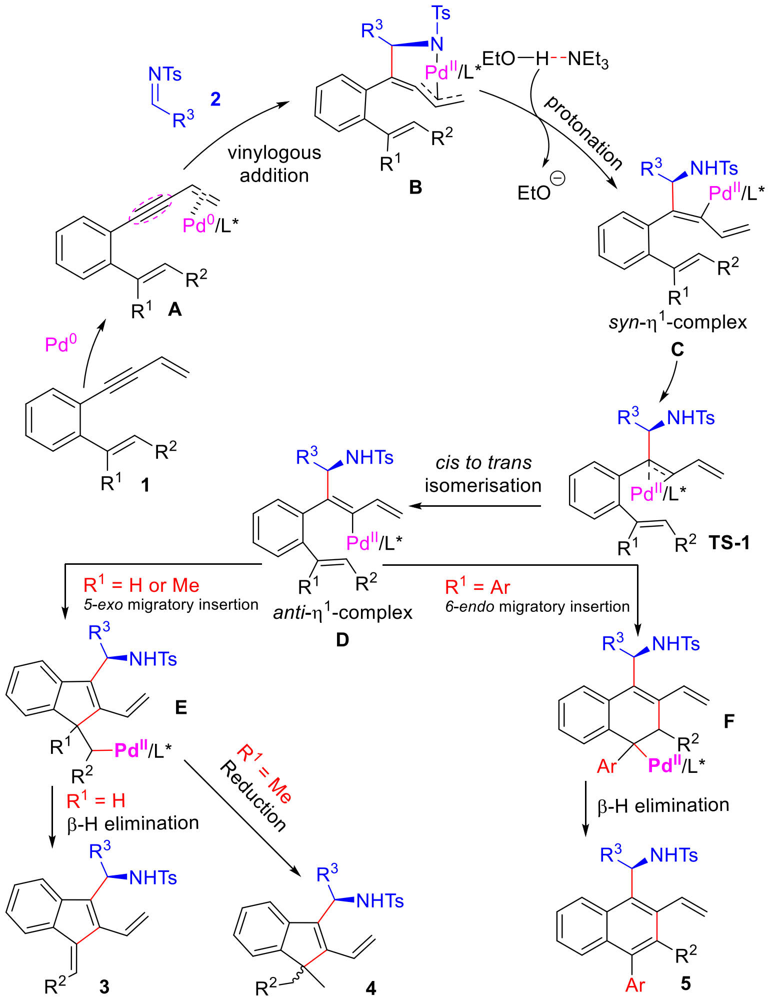
Treatment of **3j** in toluene at high temperature, the expected Diels–Alder adduct could be detected but only in a very low yield.



| | | | | |
|---|---|---|---|---|
| **Condition A** | $\xrightarrow[\text{ultrasonic}]{\text{Mg, MeOH}}$ | NR | NR | messy |
| **Condition B** | $\xrightarrow[\text{rt}]{\text{TFA/thioanisole}}$ | messy | messy | messy |
| **Condition C** | $\xrightarrow[\text{MeOH, rt–50 °C}]{\text{CuCl, NaBH}_4}$ | trace | NR | NR |
| **Condition D** | $\xrightarrow[\text{THF, rt–50 °C}]{\text{SmI}_2}$ | NR | NR | — |
| **Condition E** | $\xrightarrow[\text{THF, rt}]{\text{Na, Naphthalene}}$ | trace | trace | trace |
| **Condition F** | $\xrightarrow[\text{MeCN/DMF, 35 °C}]{\text{Cs}_2\text{CO}_3\text{/PhSH}}$ | NR | NR | — |

We tried several methods to remove the Ts group of racemic products **3a, 5a** and **7**, but no obvious conversions or complex reaction profiles were uniformly observed, probably due to the effect of existence of olefinic groups. Nevertheless, the *N*-Ns protected imines could be similarly applied, which could be easily removed.

## 10. Proposed mechanism

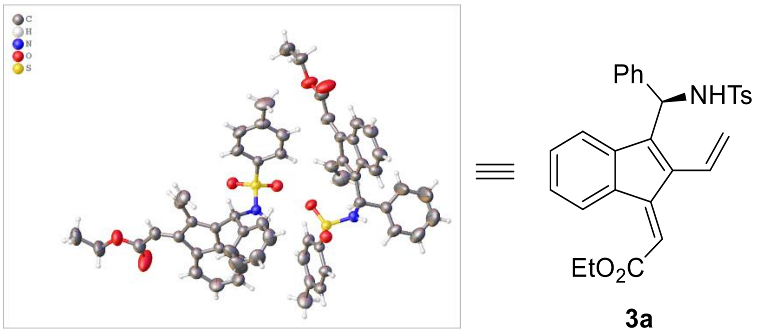


As illustrated in the above scheme, Pd$^{0}$ coordinated with the double-bond of 1,3-enyne **1** chemoseletively, and the resultant highest occupied molecular orbital (HOMO) energy raised η$^{2}$-complex **A** underwent vinylogous addition to imine **2** to produce η$^{3}$-π-allyl palladium **B**. With the assistance of triethylamine, the complex **B** would first be protonated by EtOH to deliver *syn*-alkenyl palladium **C**, which readily isomerized to thermodynamically more stable *trans*-alkenyl palladium species **D** through a three-membered ring-type transition state (**TS-1**) (*ACS Catal.*, **2020**, *10*, 10516). The *trans*-alkenyl palladium species **D** might undergo 5-*exo* migratory addition, and the resultant species **E** would readily undertake β-H elimination to afford benzofulvene derivative **3** (for R$^{1}$ = H). In addition, for intermediate **E** bearing a quaternary carbon, a reduction process might be conducted to provide densely substituted indene **4**. Nevertheless, when 1′-aryl substituted enyne was used, a *6-endo* intramolecular migratory insertion to produce **F** might be favoured, because of steric hindrance and the formation of more stable benzyl palladium complex (*Acc. Chem. Res.*, 1979, **12**, 146; *J. Am.

*Chem. Soc.,* 1974, **96**, 1133). Subsequent β-H elimination delivered skeletally different formal 1-naphthylated amine **5**.

## 11. Crystal data and structural refinement

**Procedure for the recrystallization of chiral 3a**: To a 10 mL tube containing **3a** (45 mg) were added petroleum ether (2.5 mL) and EtOAc (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure **3a**. The data were collected by Bruker D8 venture CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2249982 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



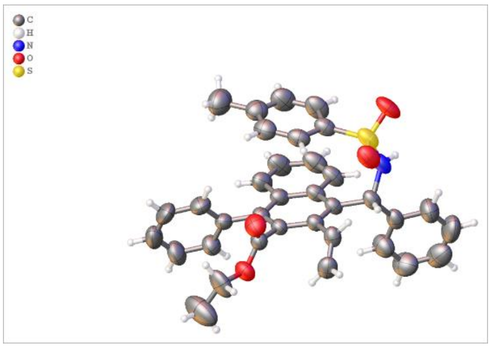
**3a**

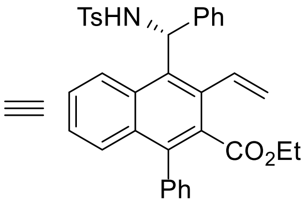
(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **3a** |
| Empirical formula | $C_{29}H_{27}NO_4S$ |
| Formula weight | 485.07 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a/Å | 9.7229(12) |
| b/Å | 26.817(4) |
| c/Å | 9.7328(16) |
| α/° | 90 |
| β/° | 90.021(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 2537.8(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.270 |
| μ/mm$^{-1}$ | 0.163 |

| | |
|---|---|
| F(000) | 1022.0 |
| Crystal size/mm$^3$ | 0.27 × 0.13 × 0.07 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.184 to 55.122 |
| Index ranges | $-11 \le h \le 12, -34 \le k \le 34, -12 \le l \le 12$ |
| Reflections collected | 26114 |
| Independent reflections | 11495 [$R_{int} = 0.0530$, $R_{sigma} = 0.0690$] |
| Data/restraints/parameters | 11495/1/635 |
| Goodness-of-fit on F$^2$ | 1.067 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0558$, $wR_2 = 0.1070$ |
| Final R indexes [all data] | $R_1 = 0.0922$, $wR_2 = 0.1241$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.22/-0.32 |
| Flack parameter | -0.06(5) |

**Procedure for the recrystallization of racemic 5r**: To a 10 mL tube containing **5r** (50 mg) were added petroleum ether (3.5 mL) and EtOAc (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of **5r**. The data were collected by Bruker D8 venture CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 302.0 K. CCDC 2249983 (*rac*-**5r**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The absolute configuration of chiral **5r** was assigned by similar vinylogous addition reaction with regard to enantiopure product **3a**.





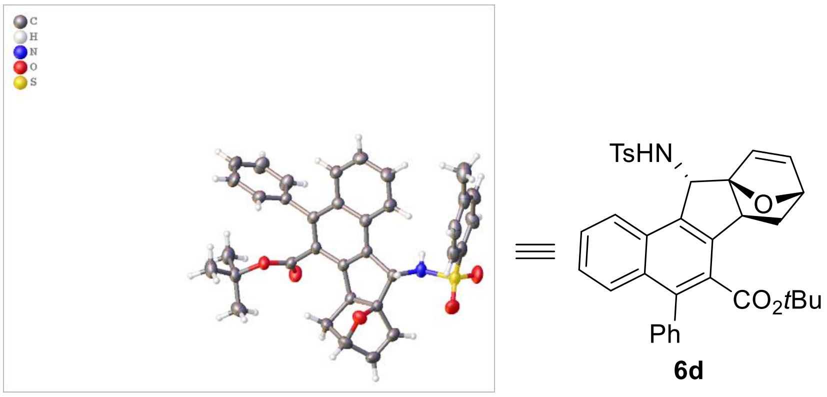
**5r**

(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **5r** |
| Empirical formula | $C_{35}H_{31}NO_4S$ |
| Formula weight | 562.715 |
| Temperature/K | 302.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |

| | |
|---|---|
| a/Å | 13.7631(11) |
| b/Å | 18.1396(15) |
| c/Å | 12.0870(11) |
| α/° | 90 |
| β/° | 95.186(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 3005.3(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.244 |
| μ/mm$^{-1}$ | 0.147 |
| F(000) | 1189.0 |
| Crystal size/mm$^3$ | 0.25 × 0.23 × 0.08 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.06 to 55.02 |
| Index ranges | $-14 \leq h \leq 17$, $-23 \leq k \leq 23$, $-12 \leq l \leq 15$ |
| Reflections collected | 20675 |
| Independent reflections | 6812 [$R_{int}$ = 0.0695, $R_{sigma}$ = 0.0811] |
| Data/restraints/parameters | 6812/6/372 |
| Goodness-of-fit on F$^2$ | 1.088 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0676, $wR_2$ = 0.1500 |
| Final R indexes [all data] | $R_1$ = 0.1498, $wR_2$ = 0.2040 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.47/-0.48 |

**Procedure for the recrystallization of racemic 6d**: To a 10 mL tube containing **6d** (40 mg) were added petroleum ether (2.5 mL) and $CHCl_3$ (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of product **6d**. The data were collected by Bruker D8 venture CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 240.0 K. CCDC 2249984 (*rac*-**6d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The absolute configuration of chiral **6d** was assigned by similar vinylogous addition reaction with regard to enantiopure product **3a**.

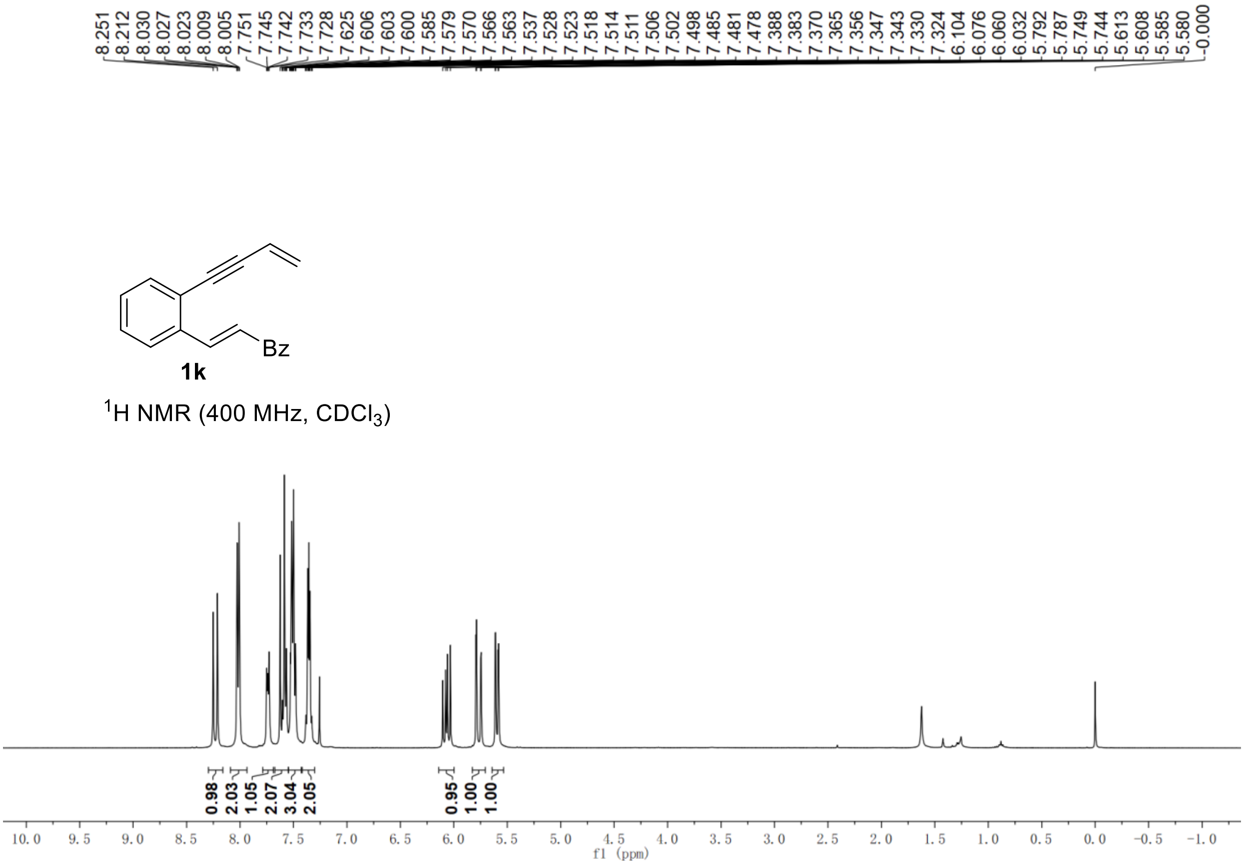


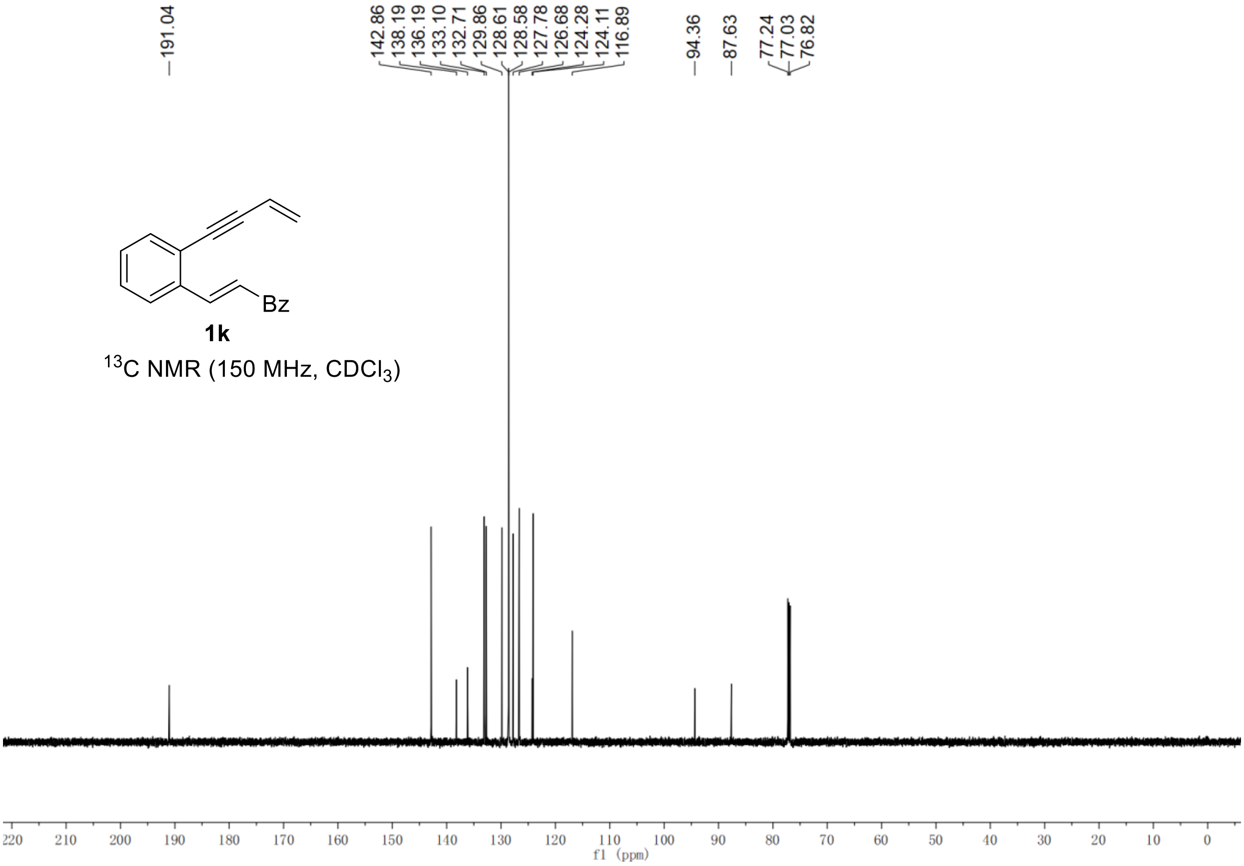
**6d**

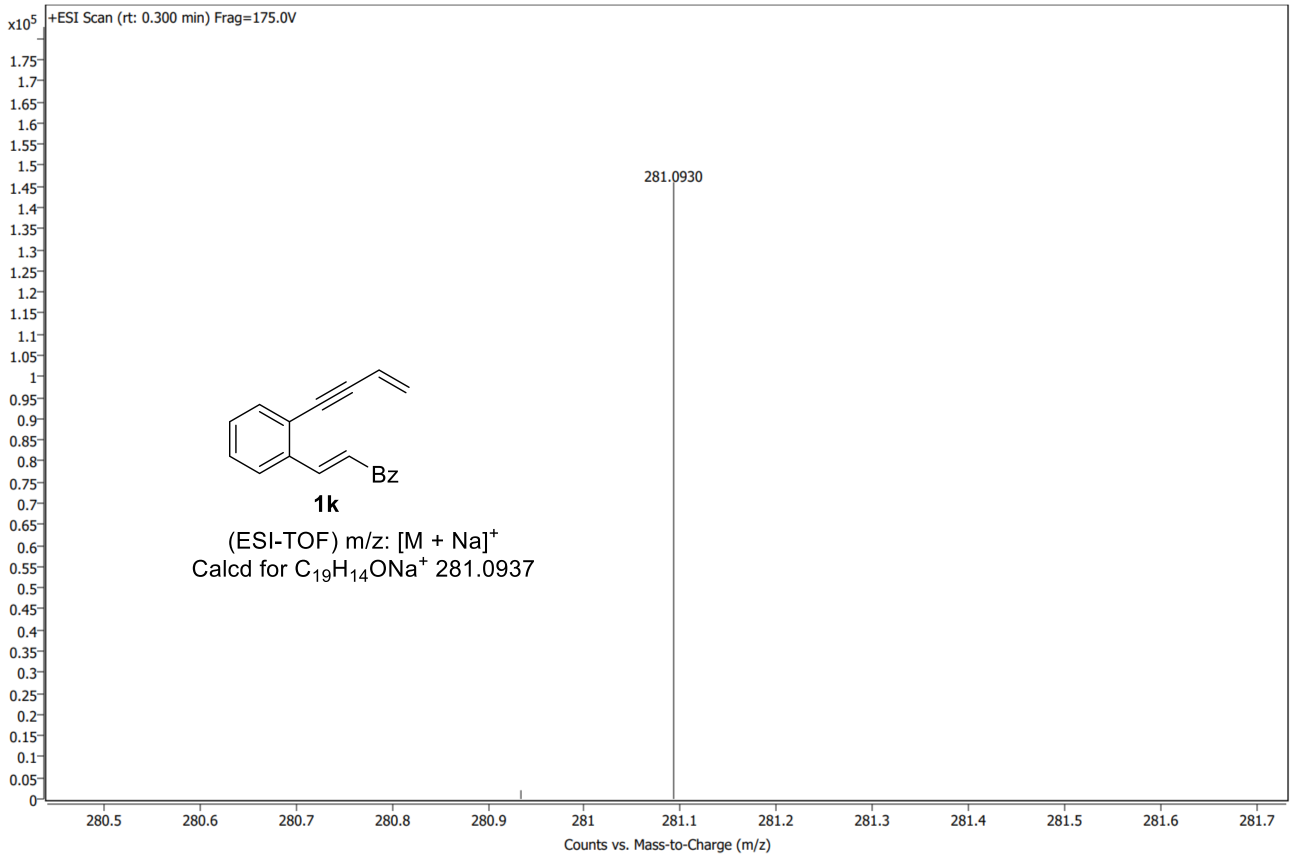
(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **6d** |
| Empirical formula | $C_{35}H_{33}NO_5S$ |
| Formula weight | 579.68 |
| Temperature/K | 240.0 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 26.644(2) |
| b/Å | 11.4614(7) |
| c/Å | 19.8518(17) |
| α/° | 90 |
| β/° | 101.614(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 5938.2(8) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.297 |
| μ/mm$^{-1}$ | 0.153 |
| F(000) | 2448.0 |
| Crystal size/mm$^3$ | 0.28 × 0.09 × 0.04 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.882 to 55.072 |
| Index ranges | $-33 \leq h \leq 34$, $-13 \leq k \leq 14$, $-25 \leq l \leq 25$ |
| Reflections collected | 32932 |
| Independent reflections | 6606 [$R_{int}$ = 0.1320, $R_{sigma}$ = 0.0984] |
| Data/restraints/parameters | 6606/0/386 |
| Goodness-of-fit on F$^2$ | 1.011 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0611, $wR_2$ = 0.1127 |
| Final R indexes [all data] | $R_1$ = 0.1363, $wR_2$ = 0.1423 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.22/-0.34 |

# 12. NMR, HRMS spectra and HPLC chromatograms



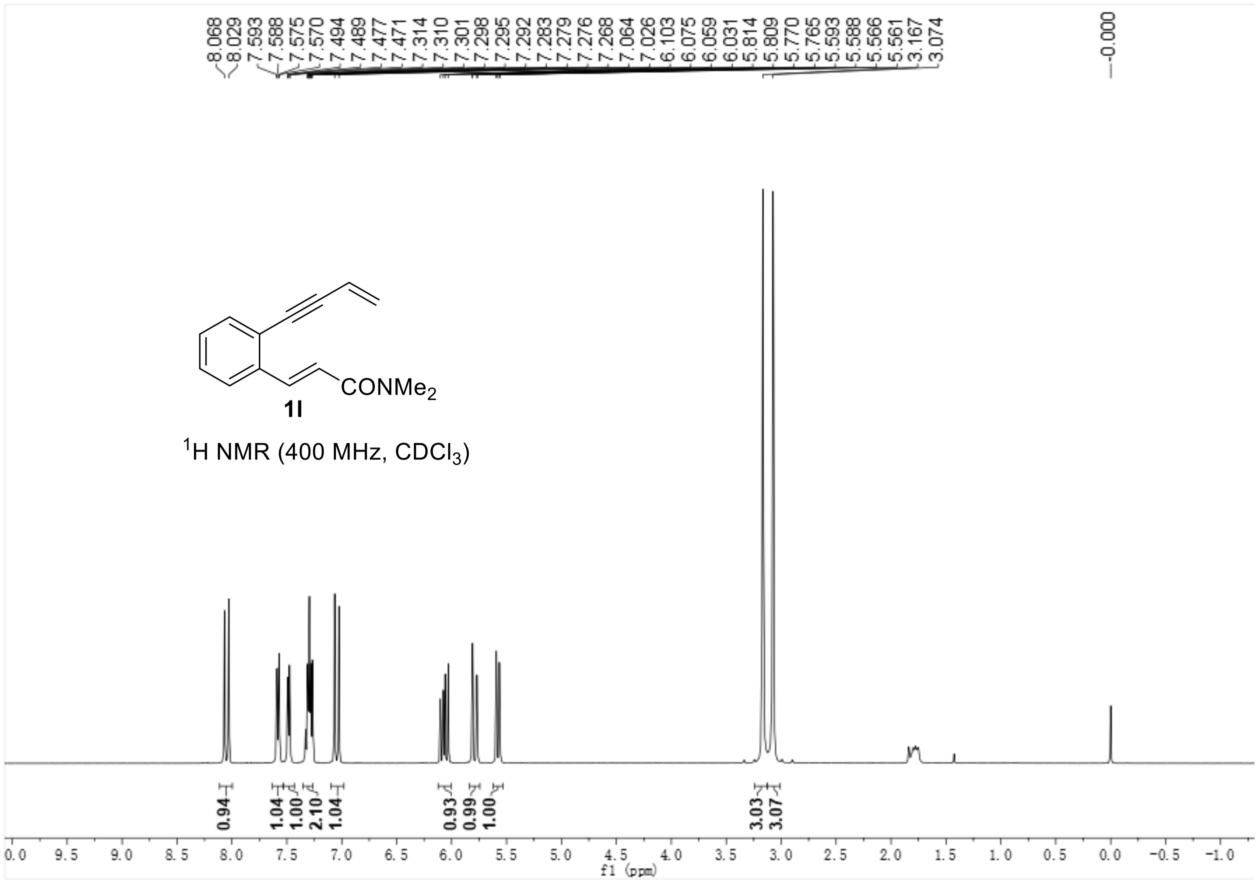


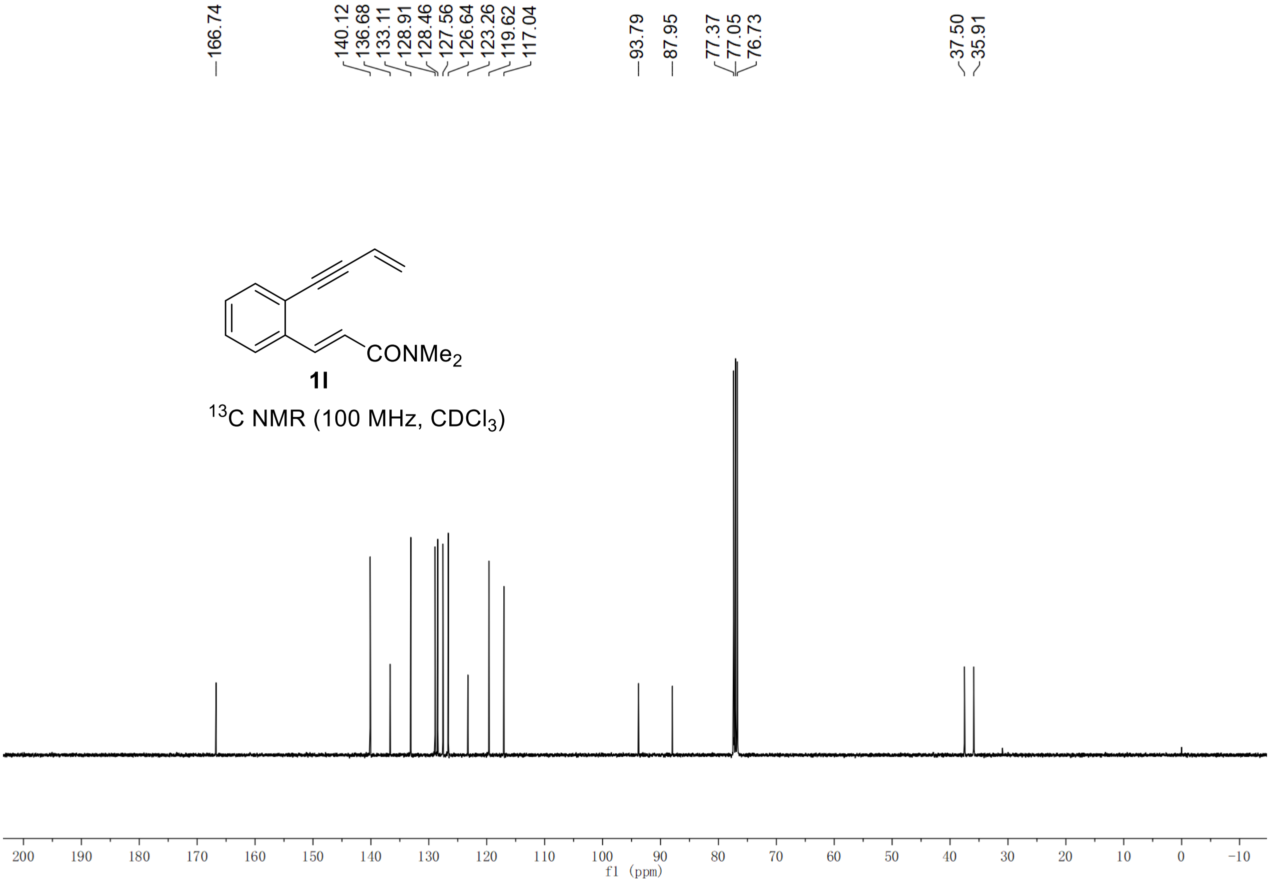


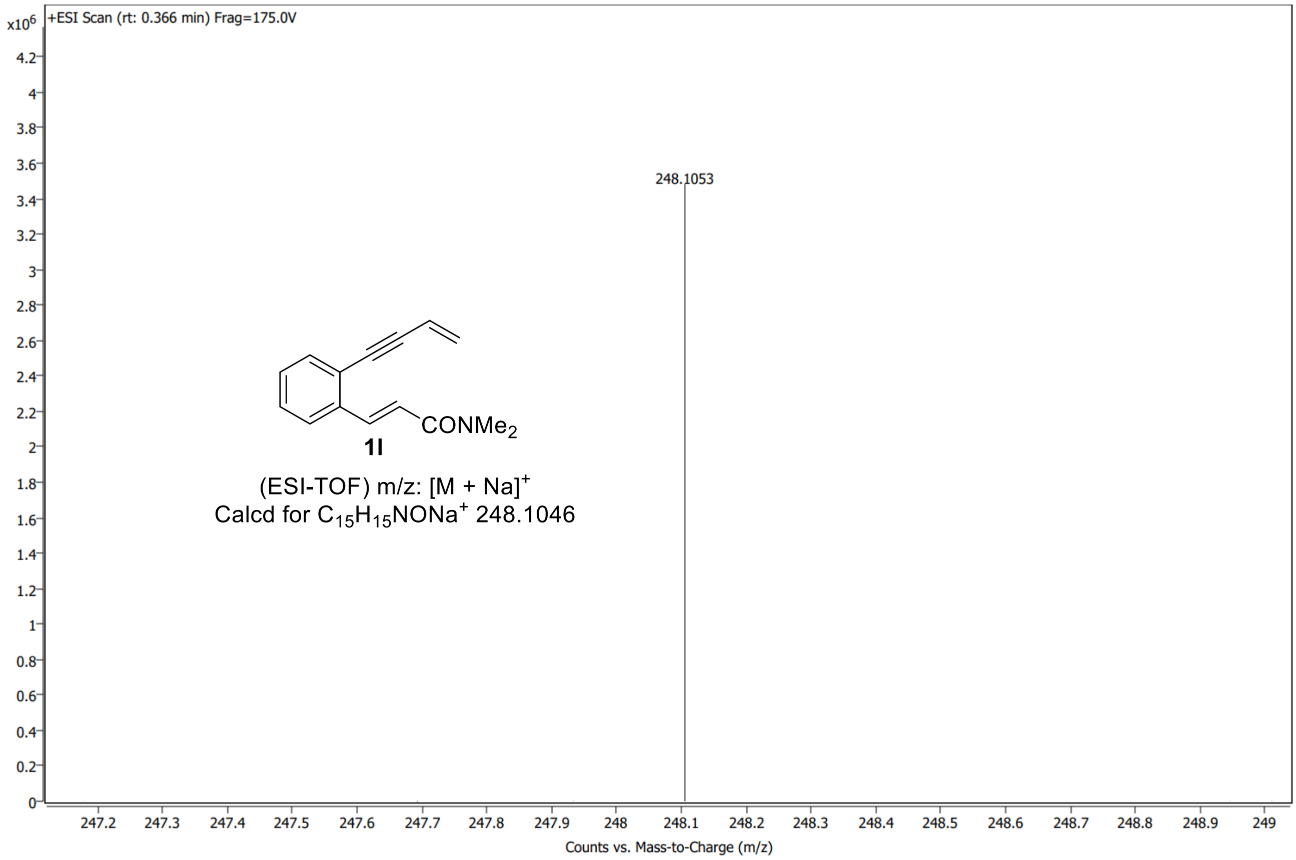
**1k**

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{19}H_{14}ONa^+$ 281.0937

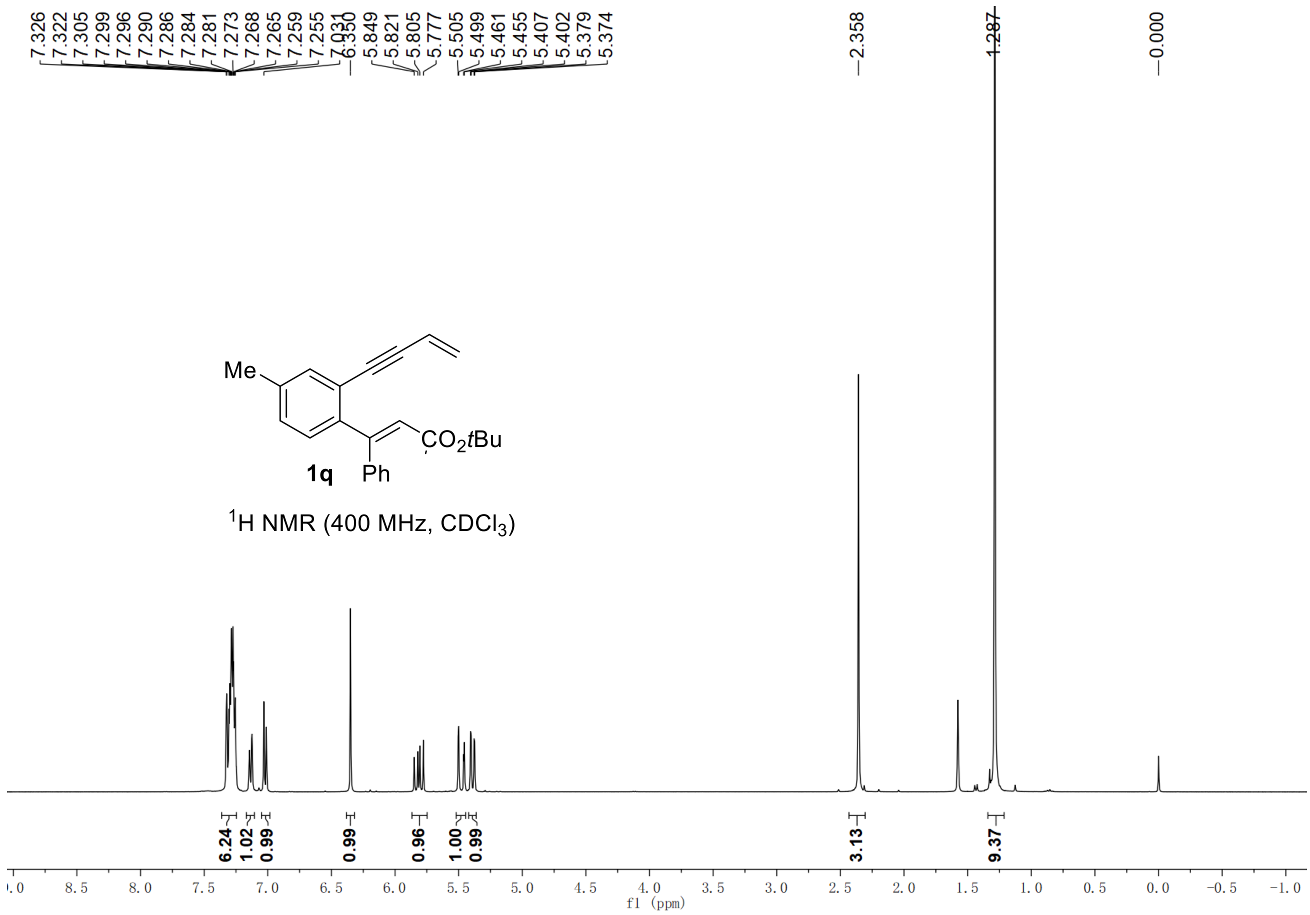

8.068
8.029
7.593
7.588
7.575
7.570
7.494
7.489
7.477
7.471
7.314
7.310
7.301
7.298
7.295
7.292
7.283
7.279
7.276
7.268
7.064
7.026
6.103
6.075
6.059
6.031
5.814
5.809
5.770
5.765
5.593
5.588
5.566
5.561
3.167
3.074
0.000
CONMe2
1l
1H NMR (400 MHz, CDCl3)
0.94
1.04
1.00
2.10
1.04
0.93
0.99
1.00
3.03
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

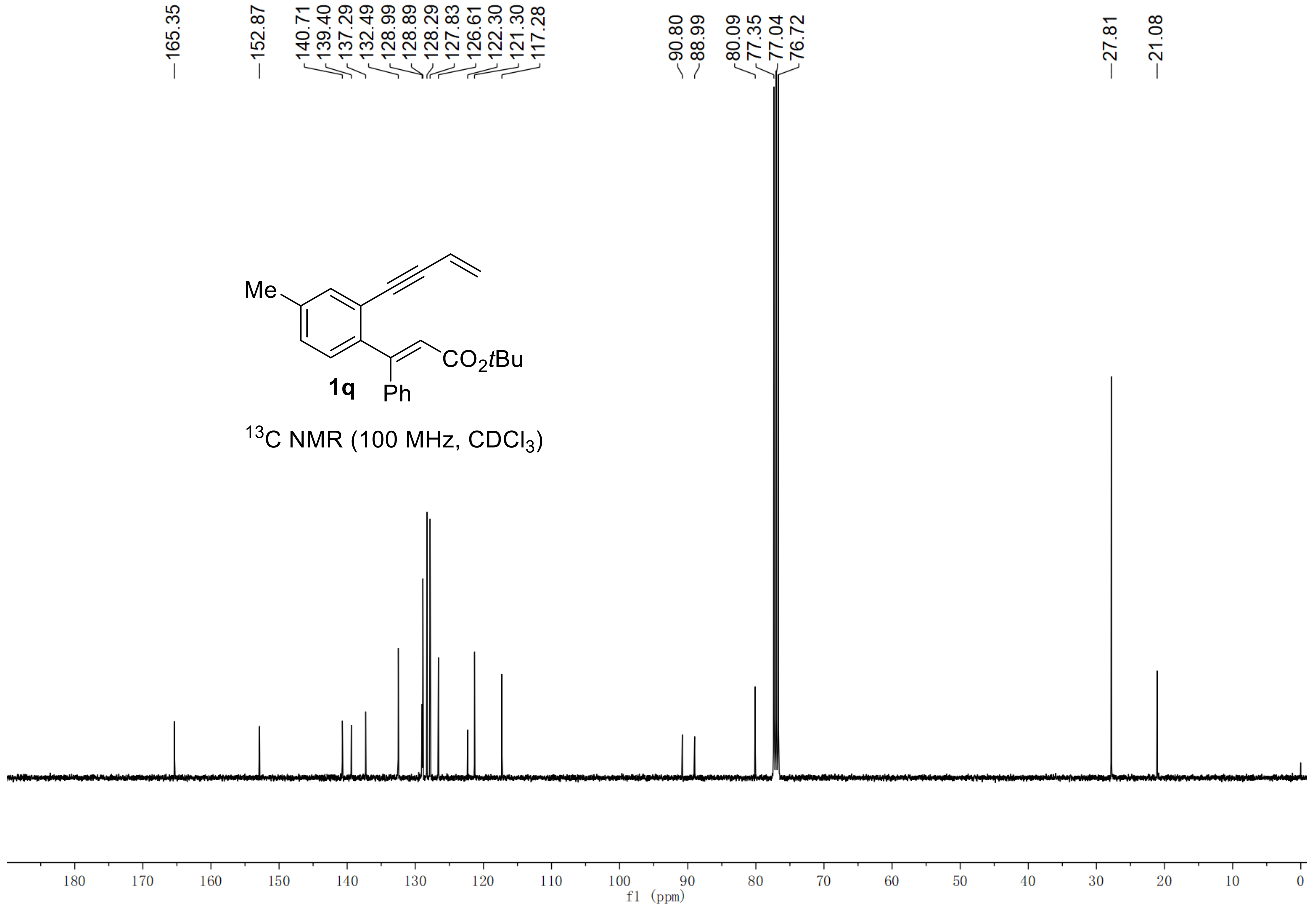

166.74
140.12
136.68
133.11
128.91
128.46
127.56
126.64
123.26
119.62
117.04
93.79
87.95
77.37
77.05
76.73
37.50
35.91
CONMe2
1l
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

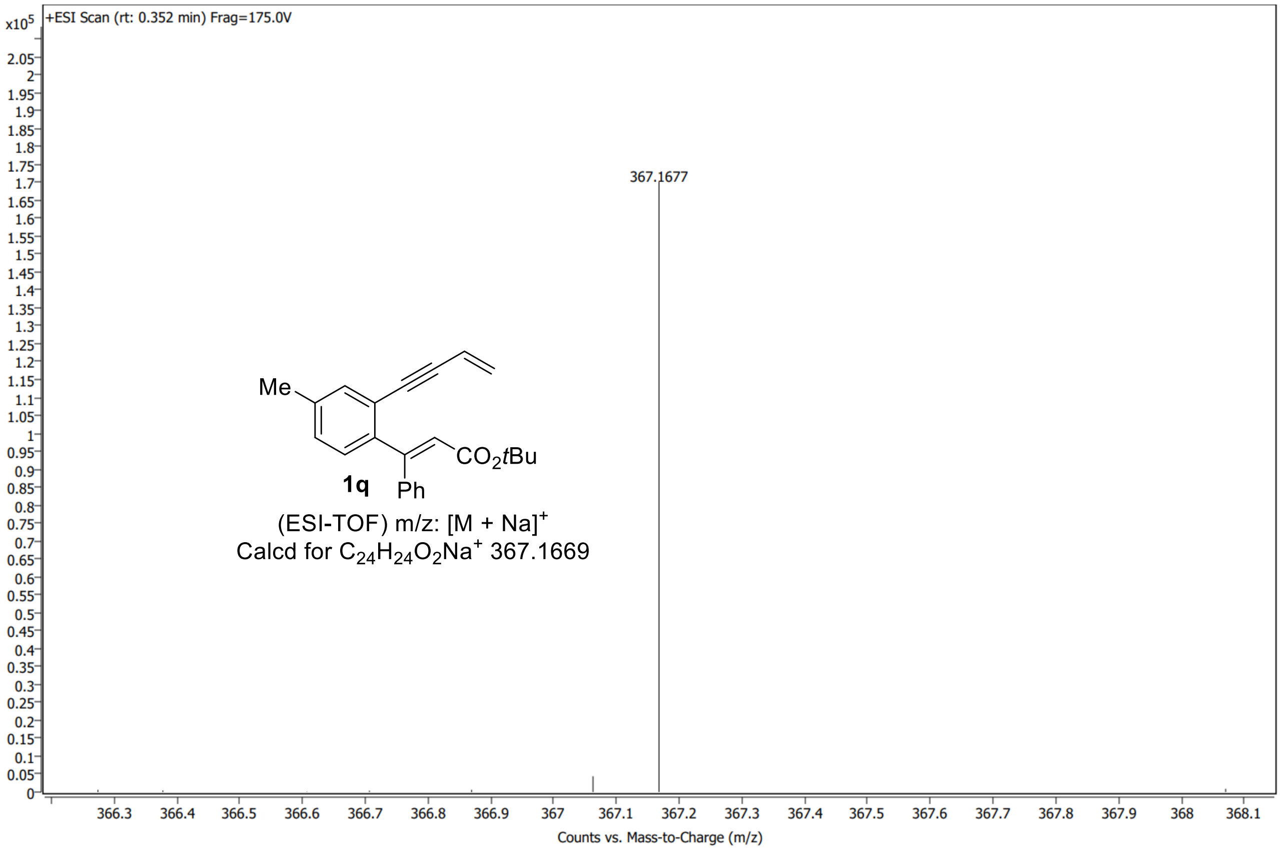


**1l**

(ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{15}H_{15}NONa^+$ 248.1046


7.326
7.322
7.305
7.299
7.296
7.290
7.286
7.284
7.281
7.273
7.268
7.265
7.259
7.255
7.031
6.350
5.849
5.821
5.805
5.777
5.505
5.499
5.461
5.455
5.407
5.402
5.379
5.374
2.358
1.287
0.000
Me
CO2tBu
1q
Ph
1H NMR (400 MHz, CDCl3)
6.24
1.02
0.99
0.99
0.96
1.00
0.99
3.13
9.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

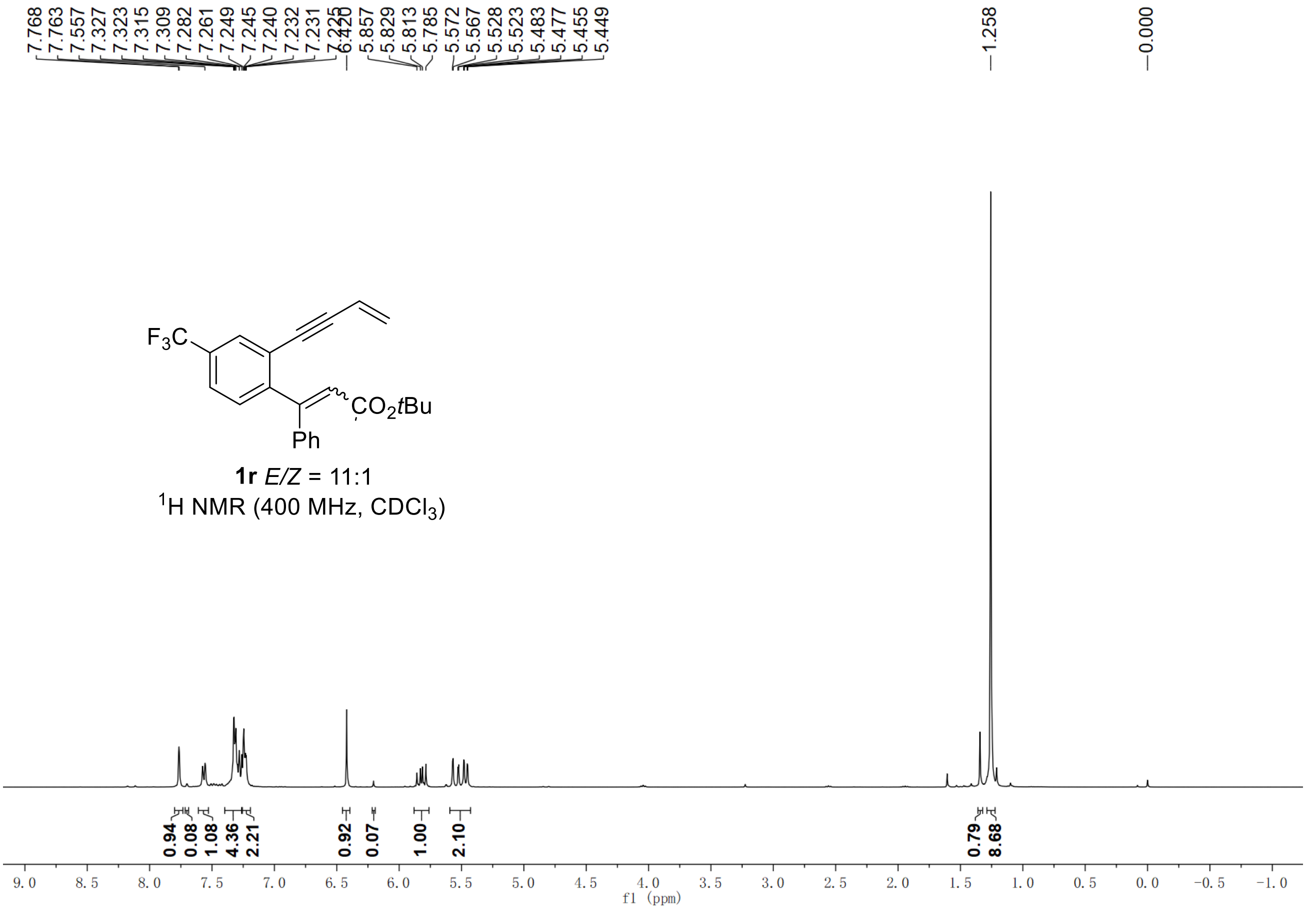

165.35
152.87
140.71
139.40
137.29
132.49
128.99
128.89
128.29
127.83
126.61
122.30
121.30
117.28
90.80
88.99
80.09
77.35
77.04
76.72
27.81
21.08
Me
CO2tBu
1q
Ph
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**1q**

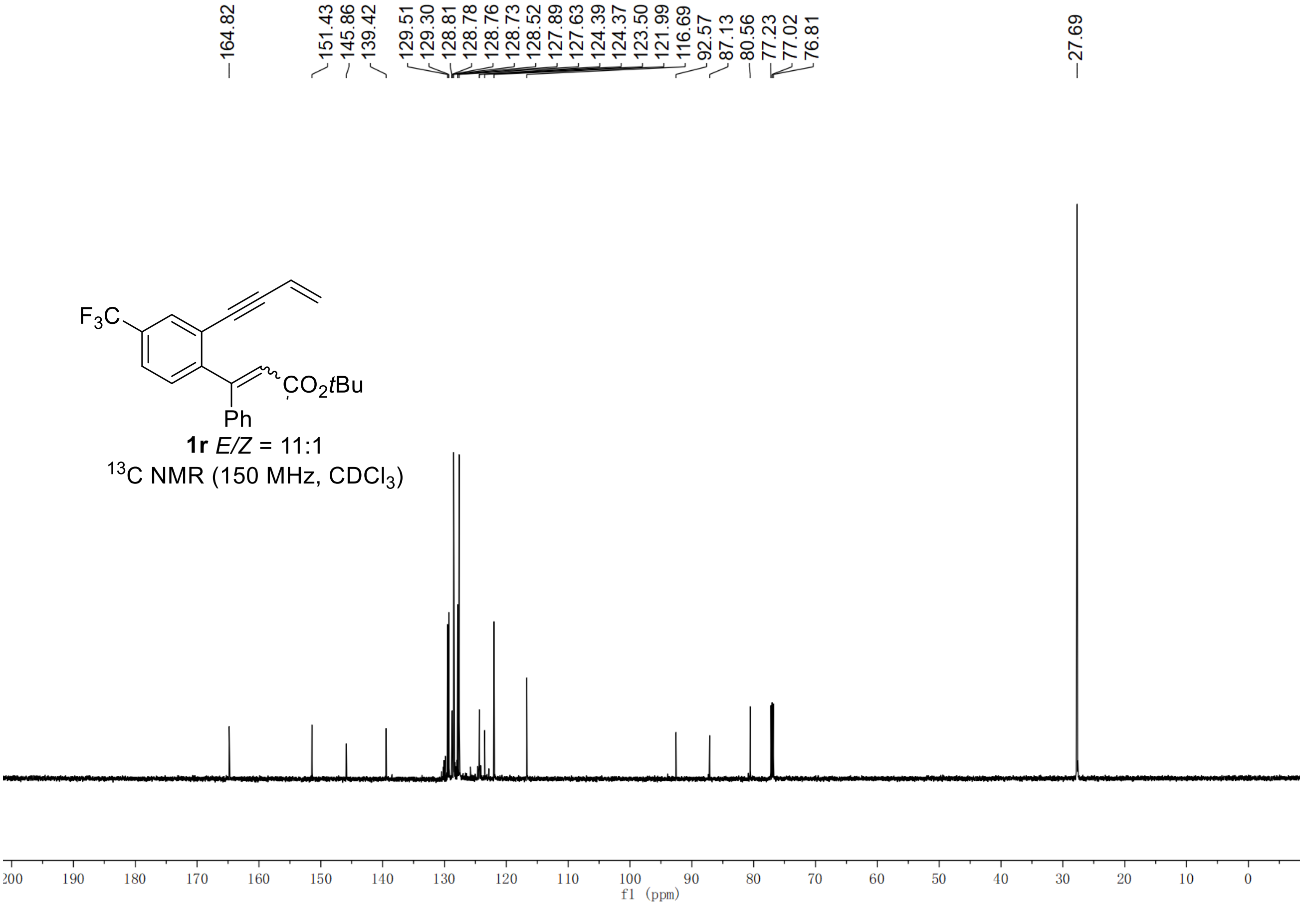
(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{24}H_{24}O_2Na^+$ 367.1669



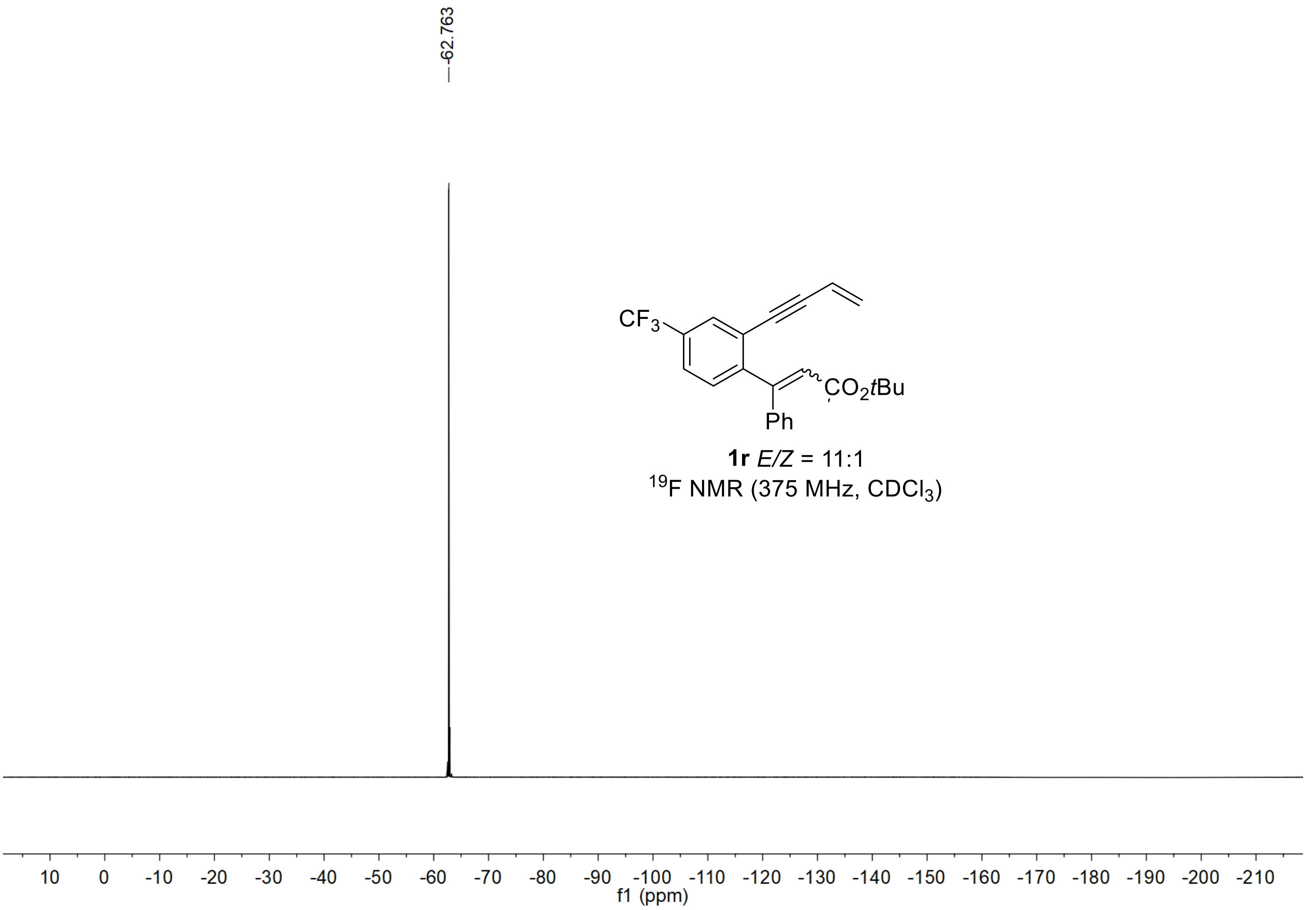
**1r** *E/Z* = 11:1

$^1$H NMR (400 MHz, CDCl$_3$)



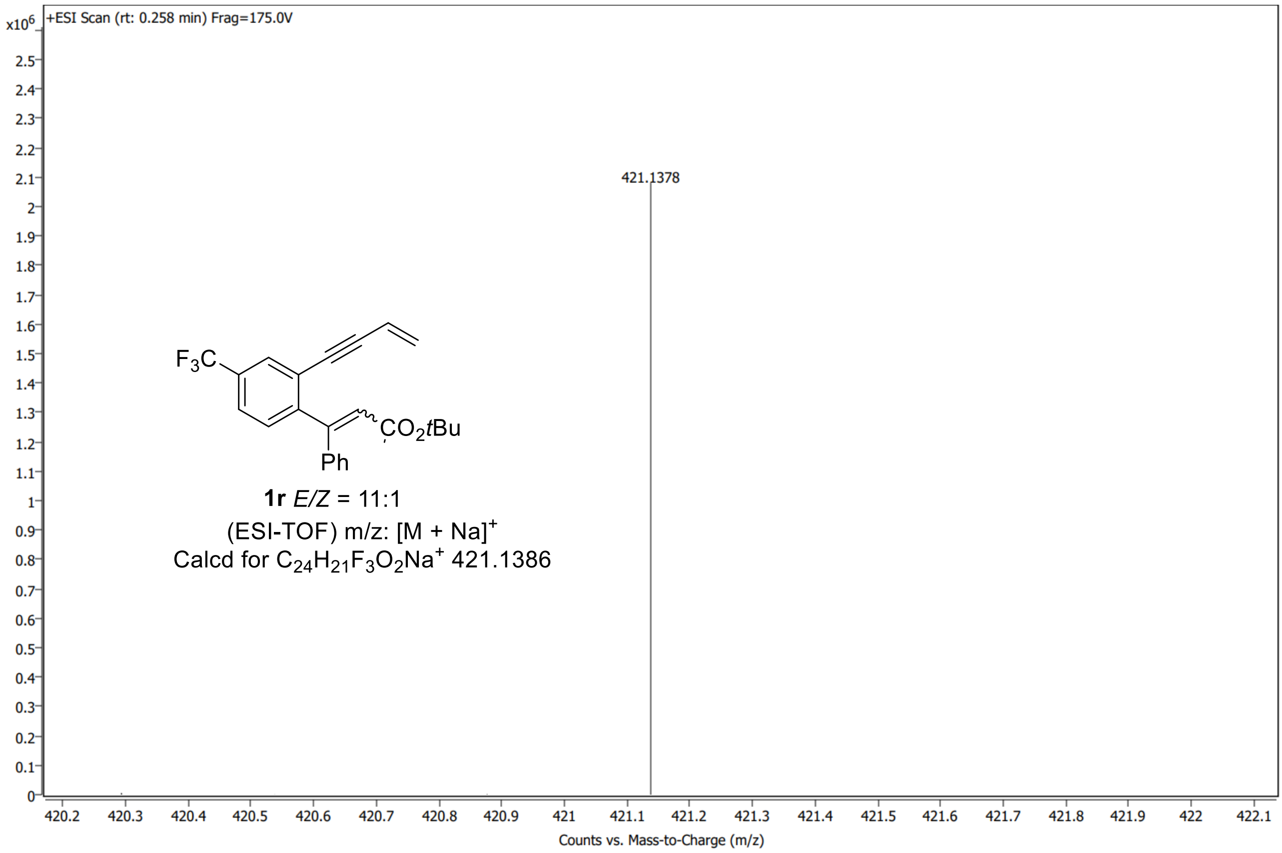
**1r** *E/Z* = 11:1

$^{13}$C NMR (150 MHz, CDCl$_3$)



**1r** *E/Z* = 11:1

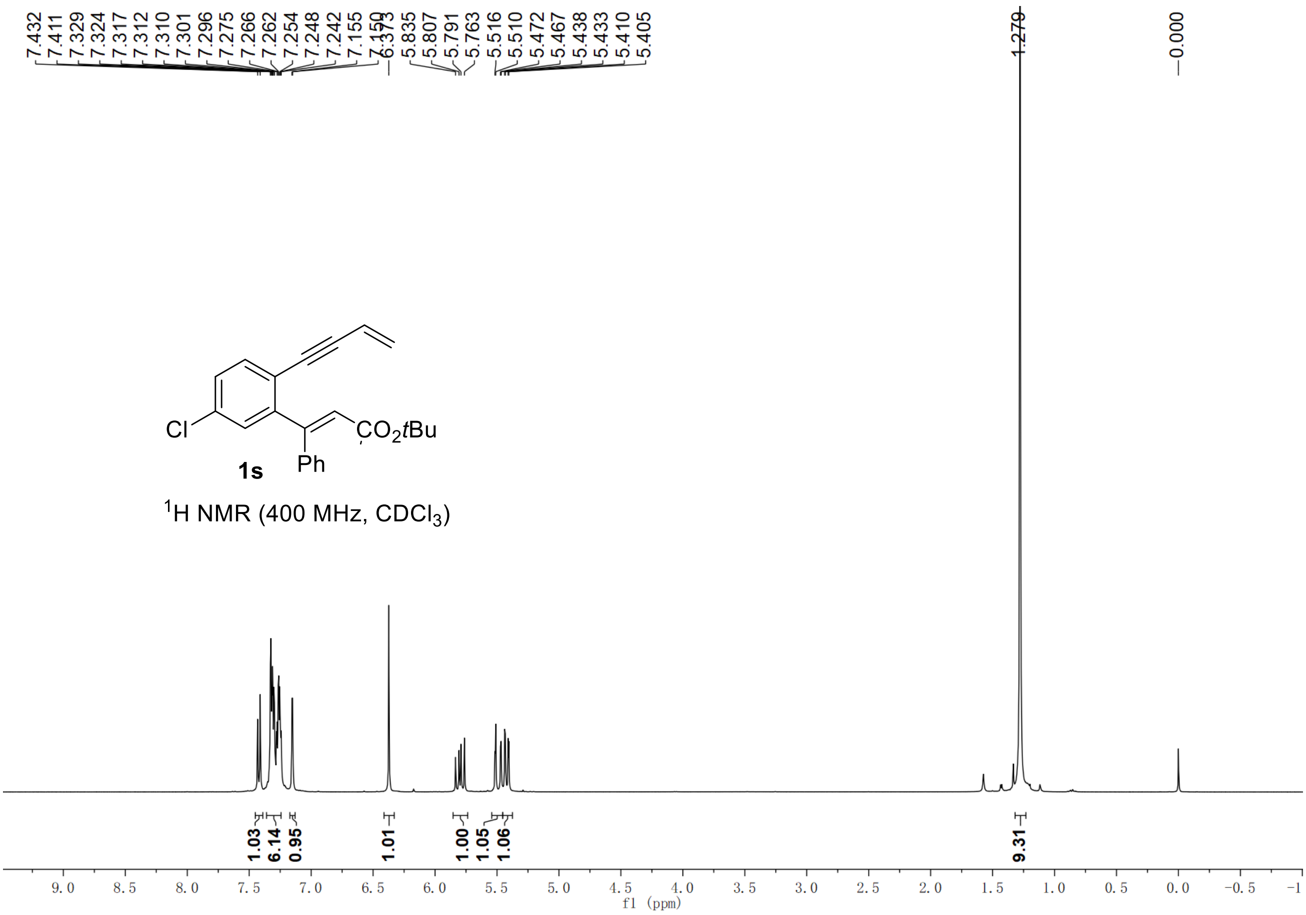
$^{19}$F NMR (375 MHz, $CDCl_3$)



**1r** *E/Z* = 11:1

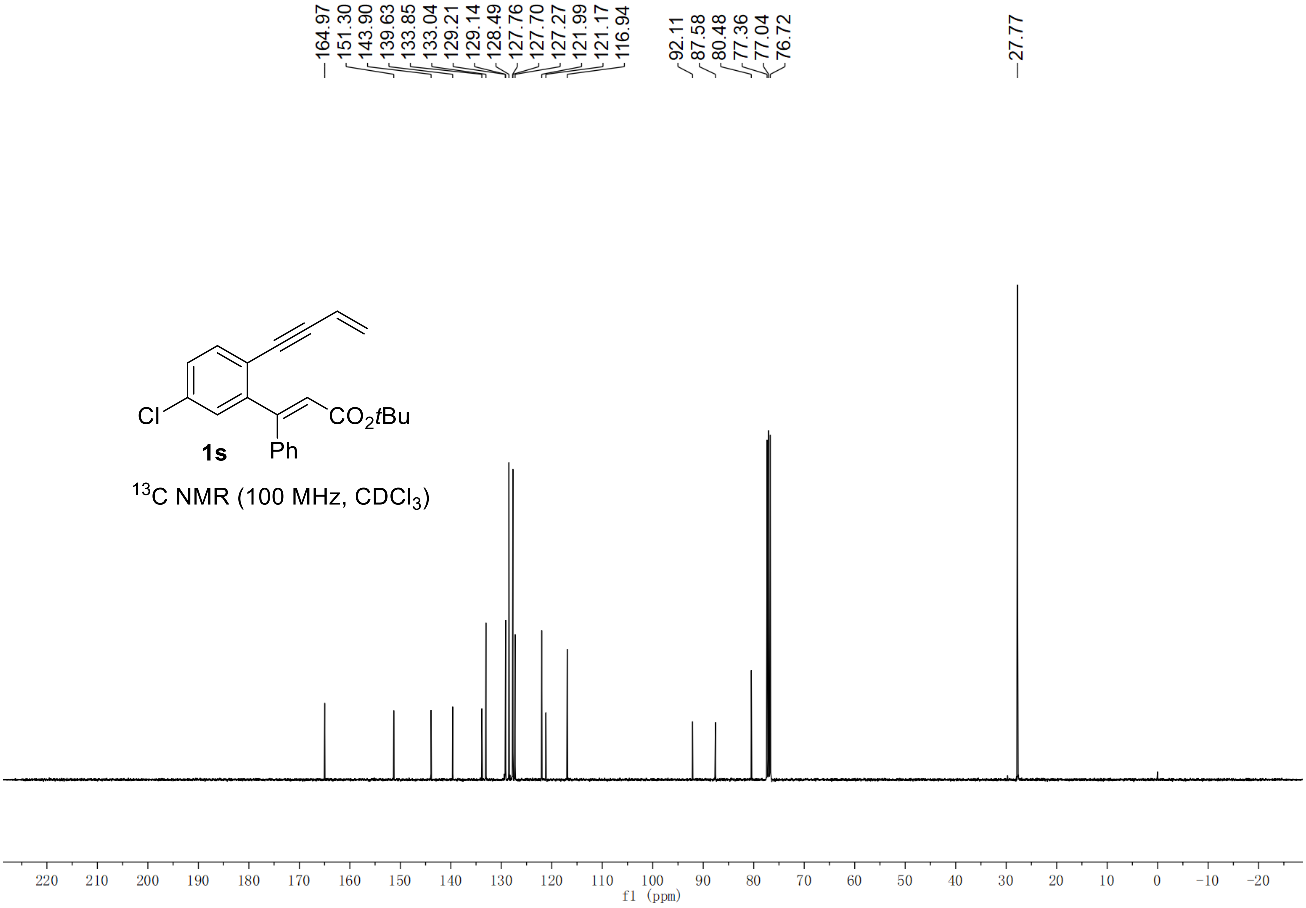
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{24}H_{21}F_3O_2Na^+$ 421.1386



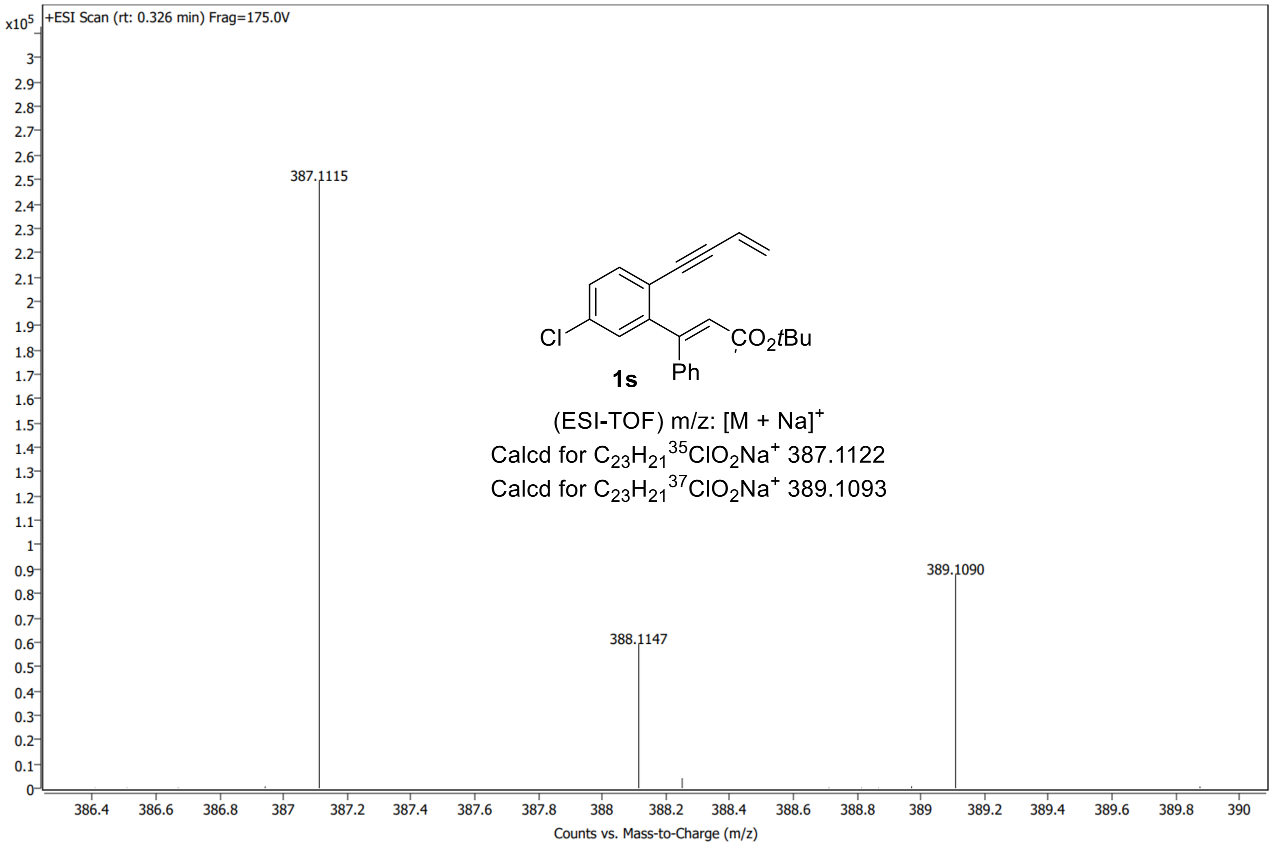
**1s**

$^1$H NMR (400 MHz, $CDCl_3$)



**1s**

$^{13}$C NMR (100 MHz, $CDCl_3$)

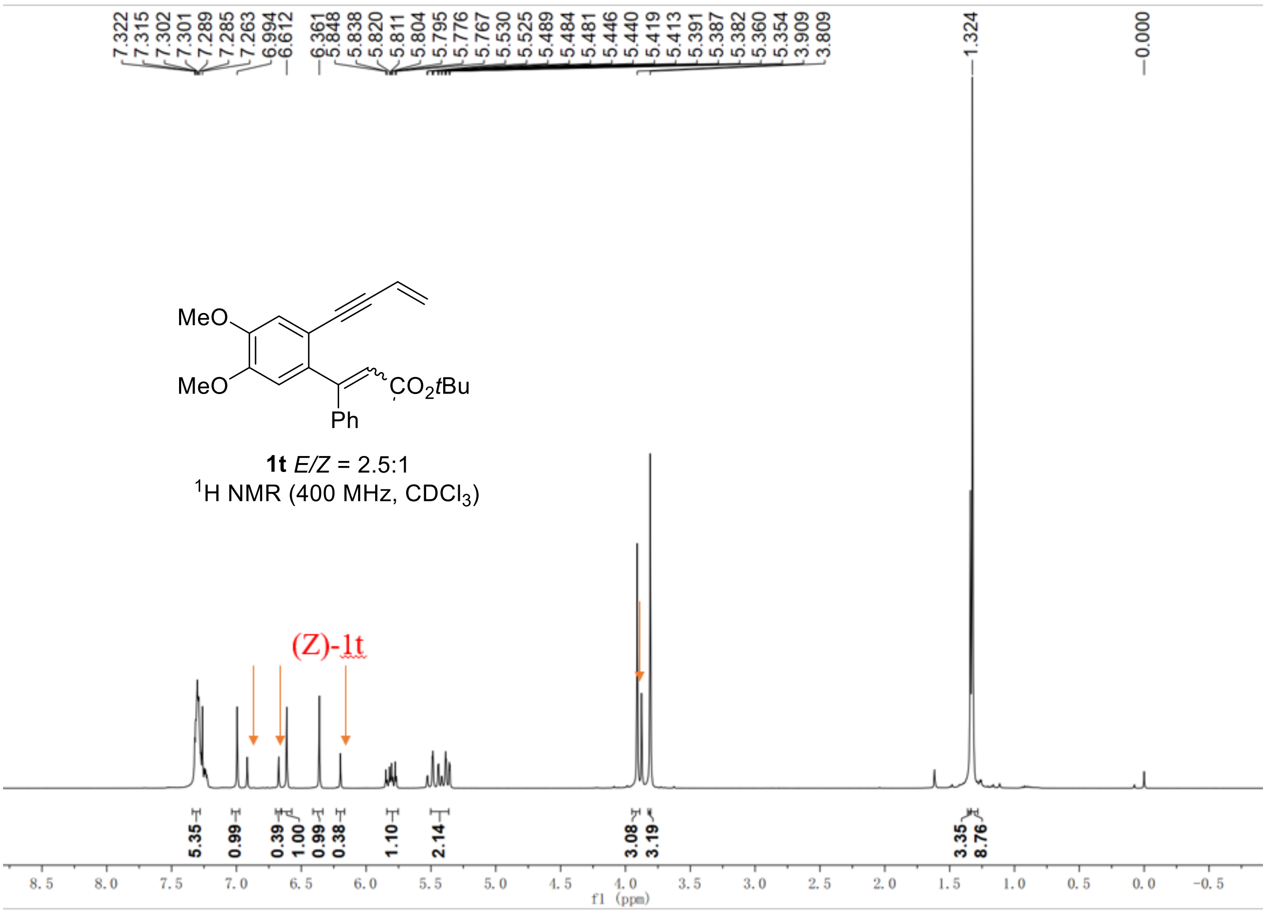


**1s**

(ESI-TOF) m/z: [M + Na]$^+$

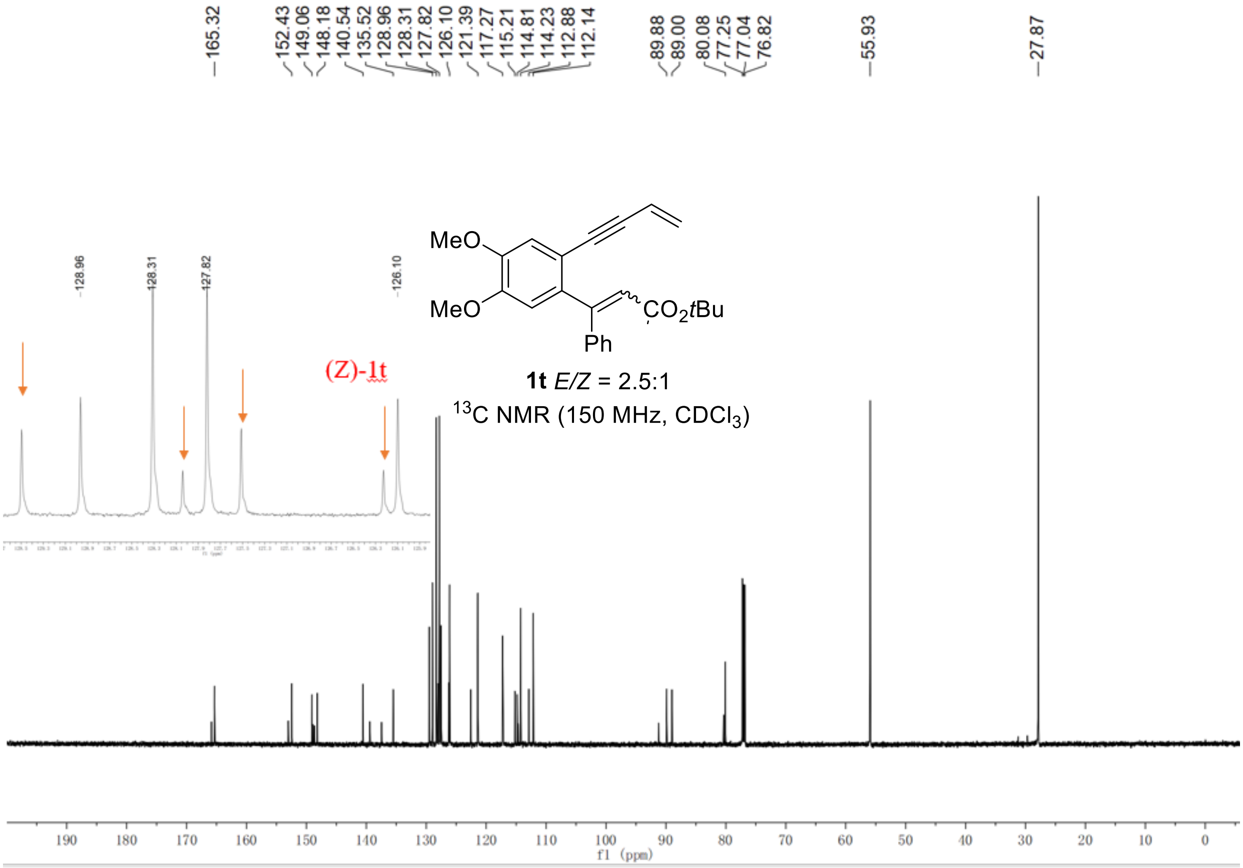
Calcd for $C_{23}H_{21}{}^{35}ClO_2Na^+$ 387.1122

Calcd for $C_{23}H_{21}{}^{37}ClO_2Na^+$ 389.1093



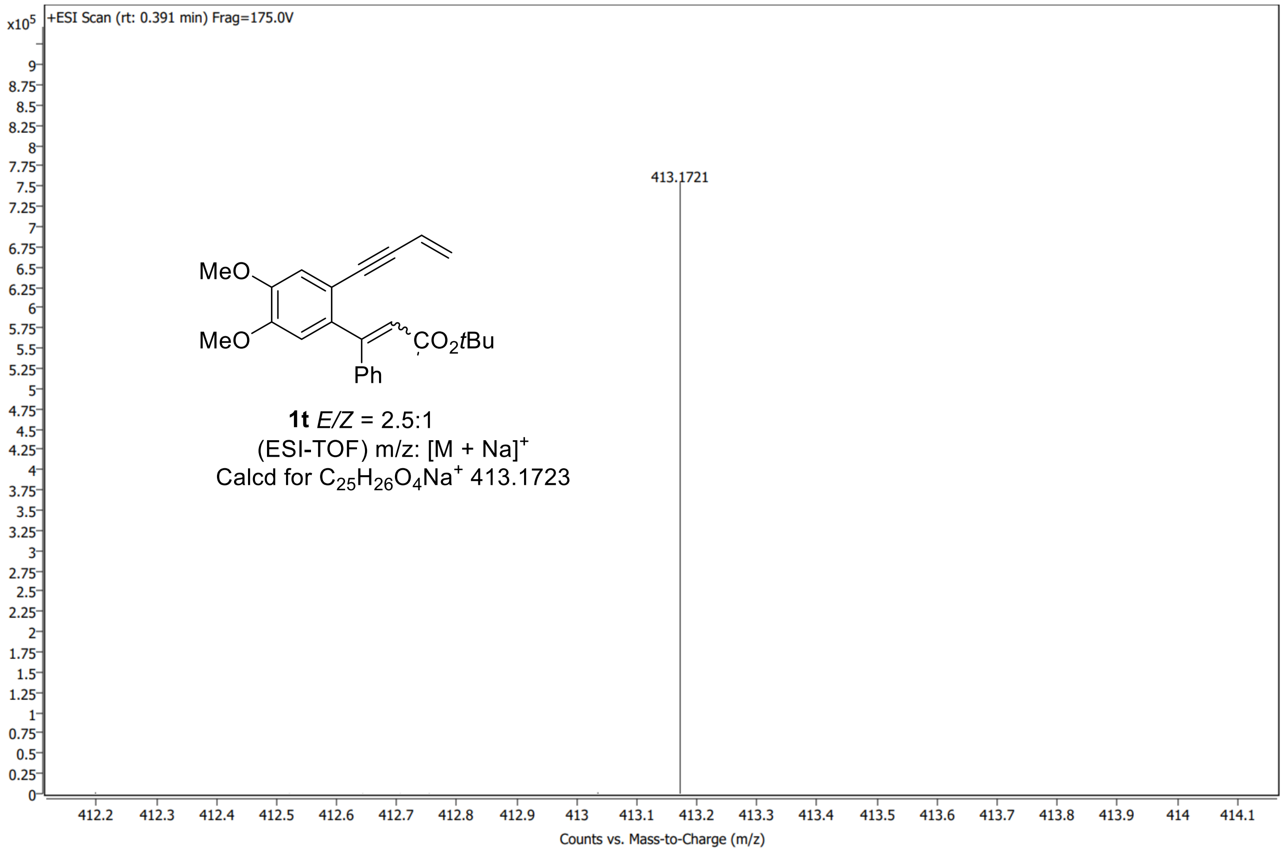
**1t** *E/Z* = 2.5:1

$^1$H NMR (400 MHz, $CDCl_3$)



**1t** *E/Z* = 2.5:1

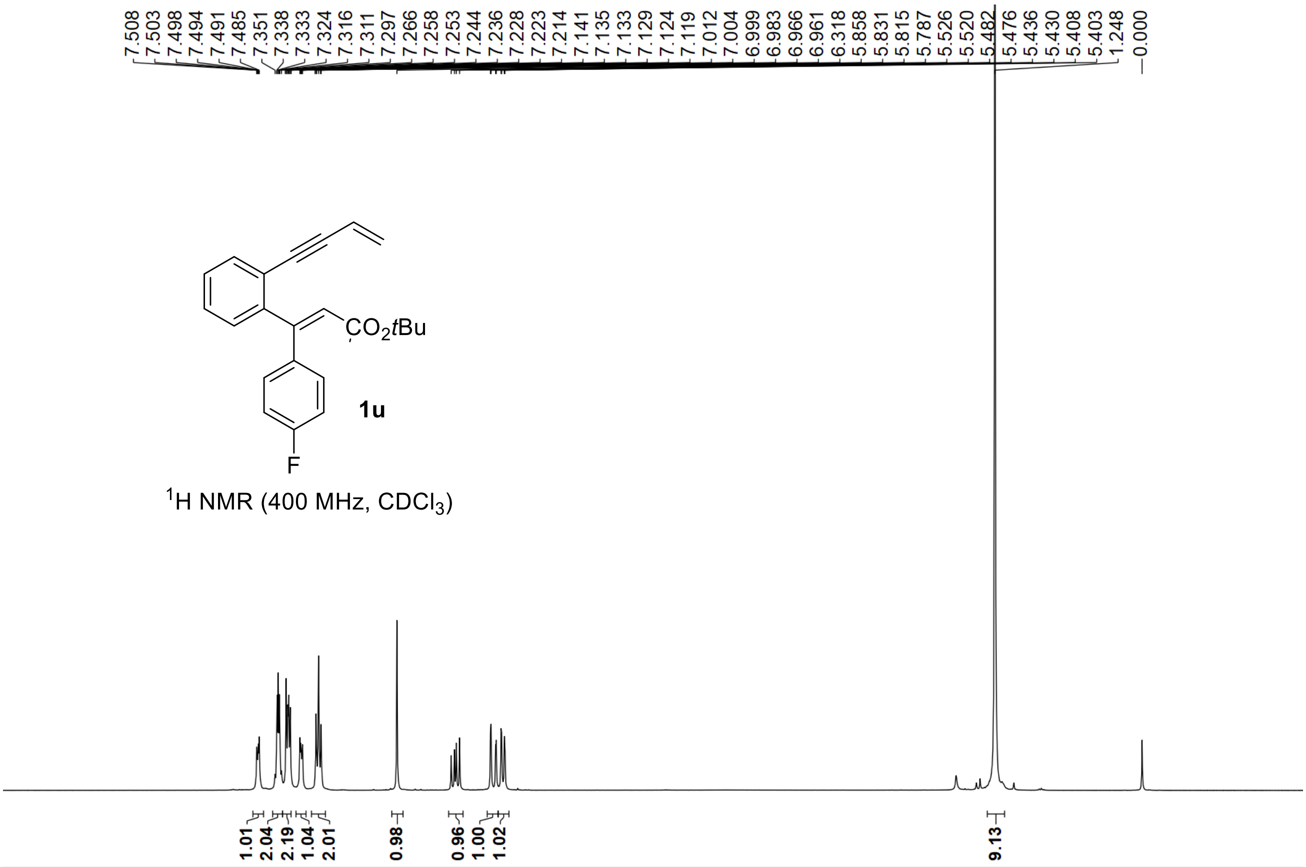
$^{13}$C NMR (150 MHz, $CDCl_3$)



**1t** *E/Z* = 2.5:1

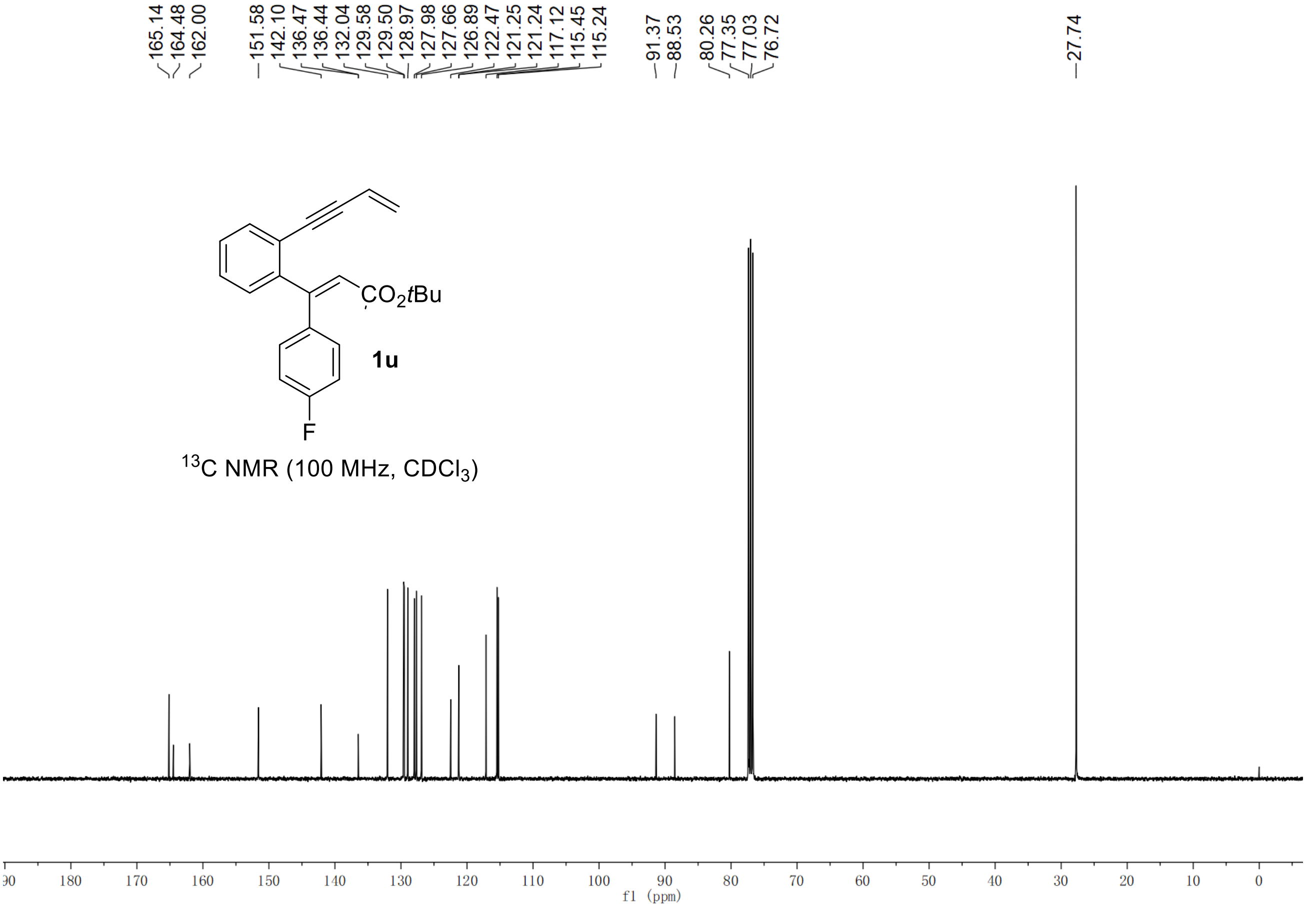
(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{25}H_{26}O_4Na^+$ 413.1723



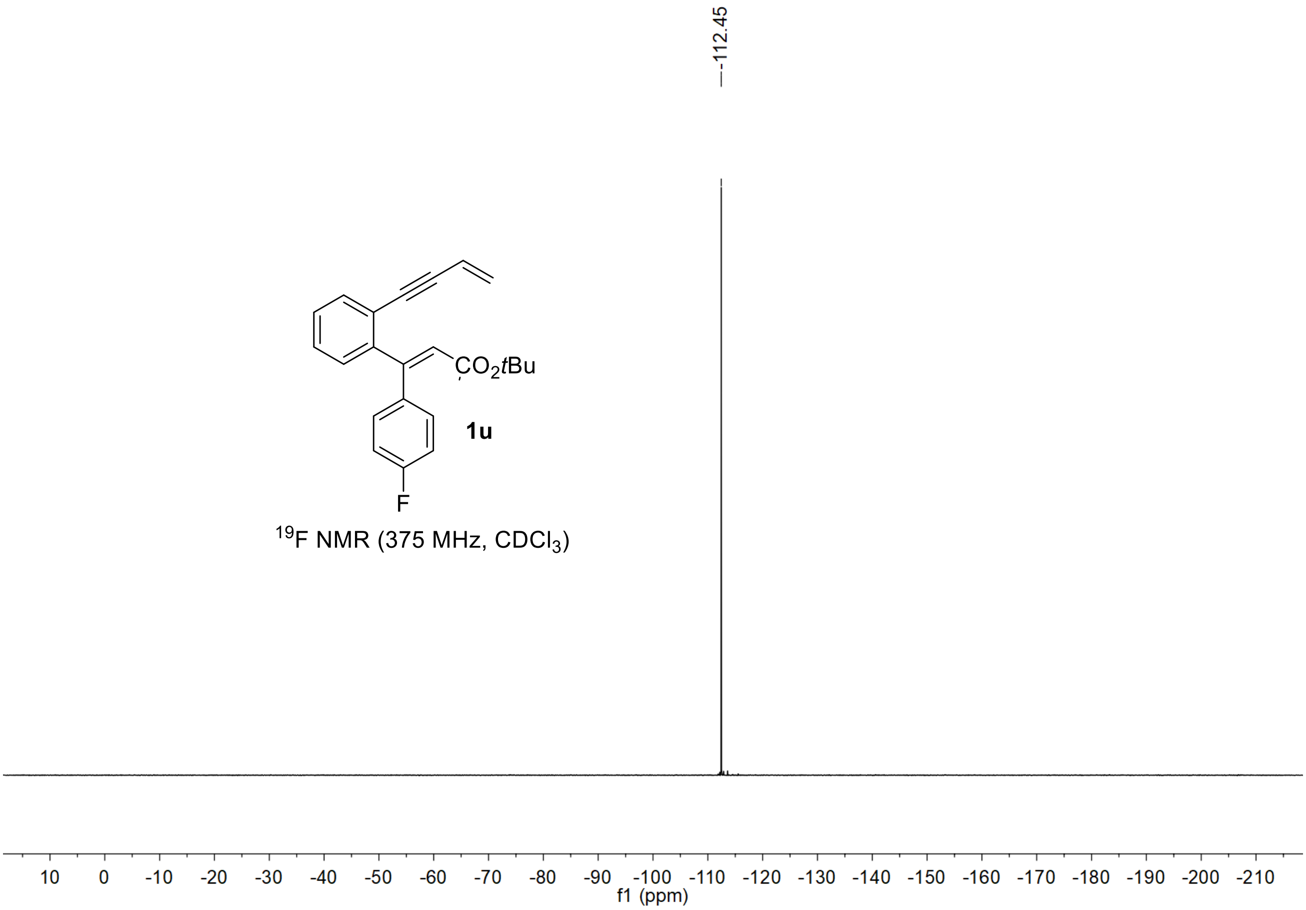
**1u**

$^1$H NMR (400 MHz, CDCl$_3$)



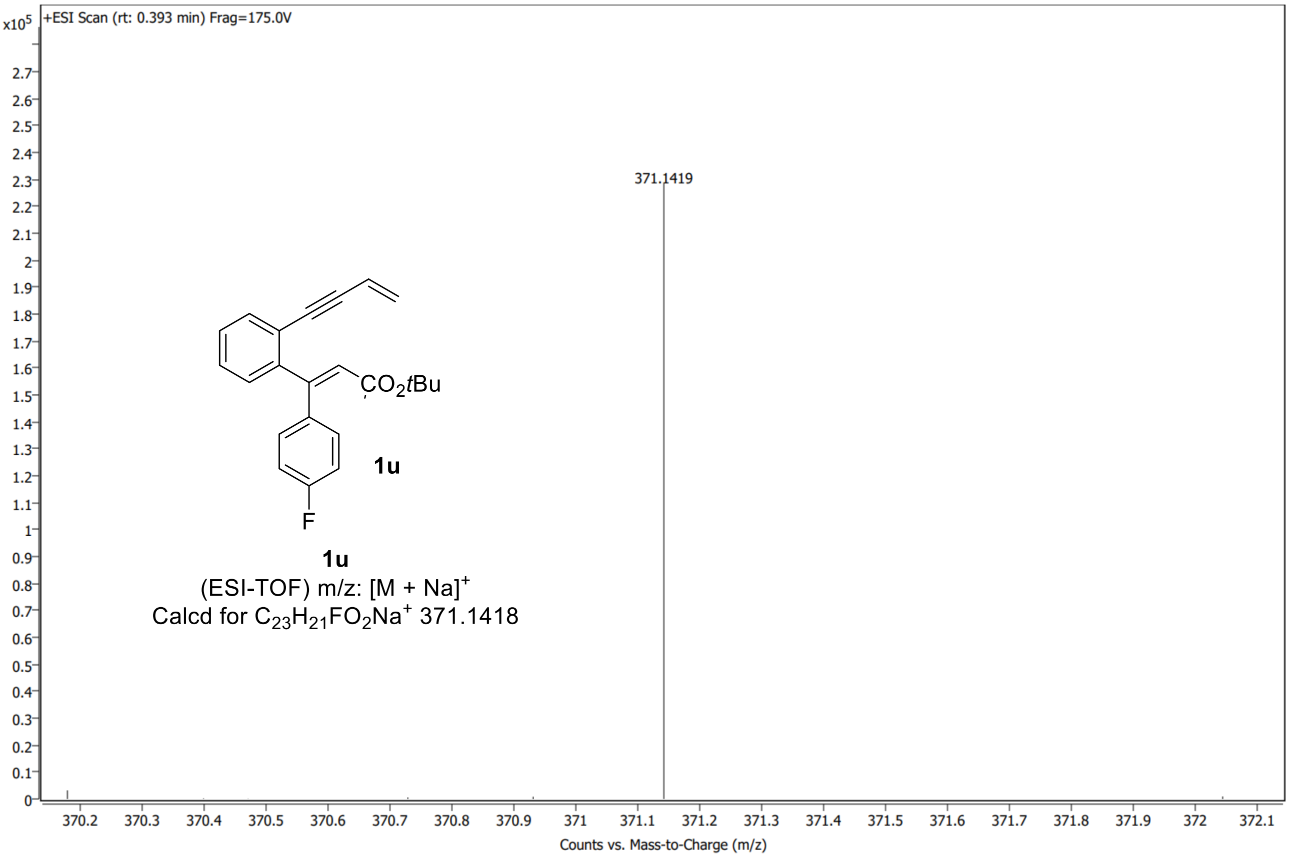
**1u**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**1u**

$^{19}$F NMR (375 MHz, $CDCl_3$)

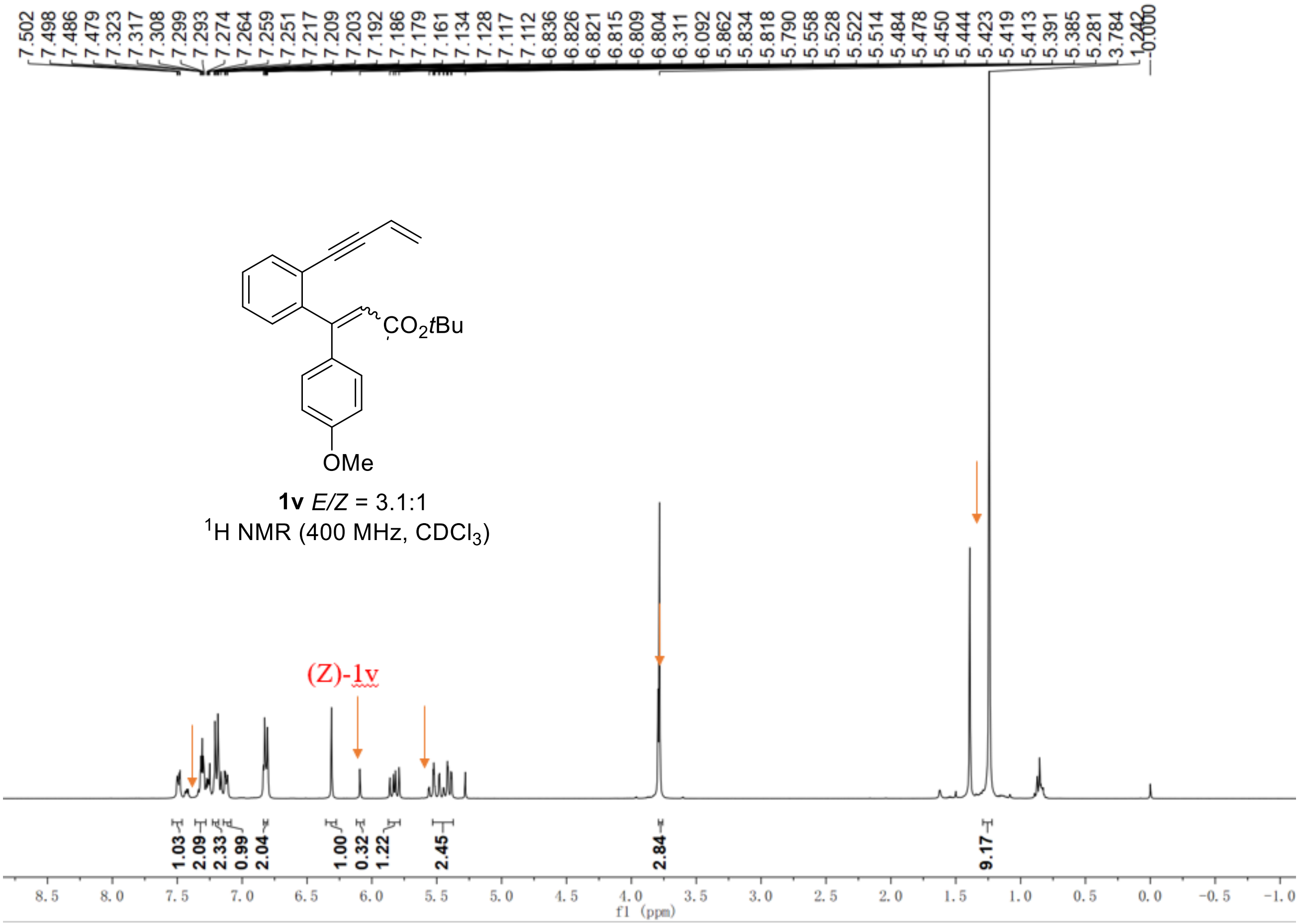


**1u**

**1u**

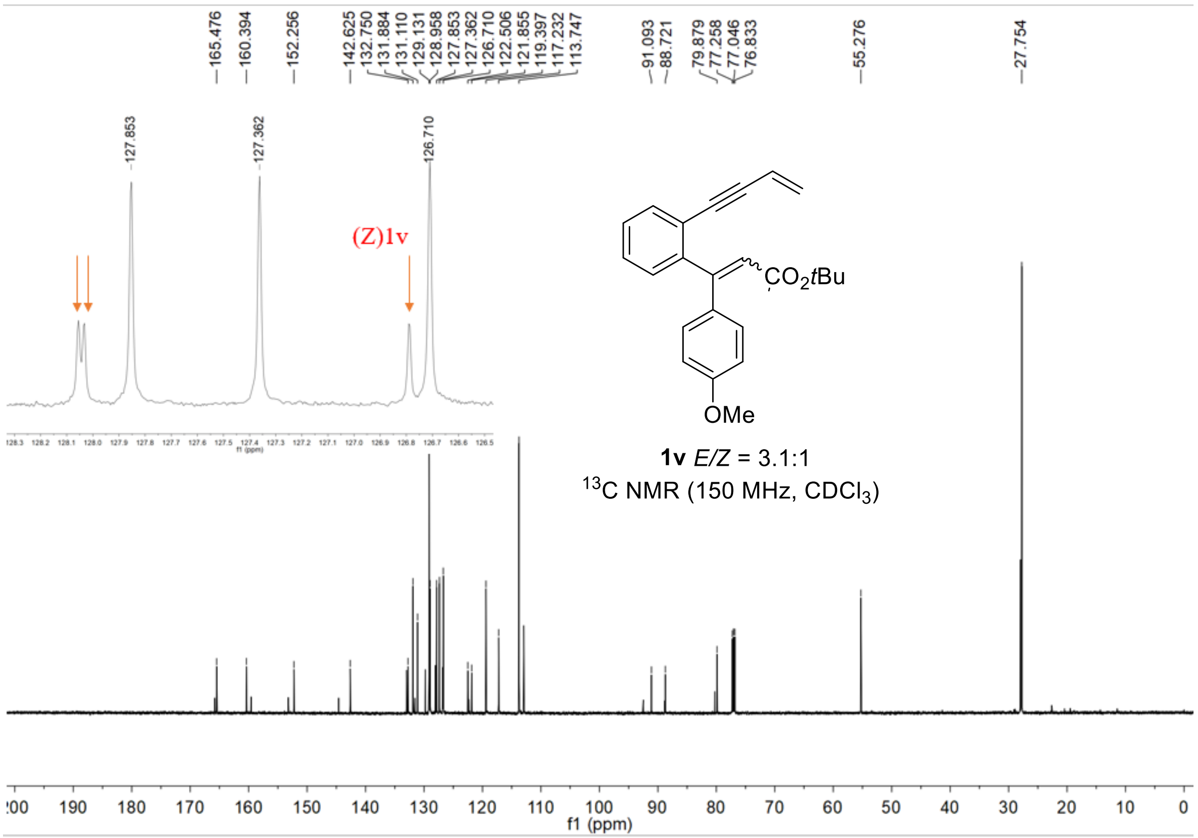
(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{23}H_{21}FO_2Na^+$ 371.1418



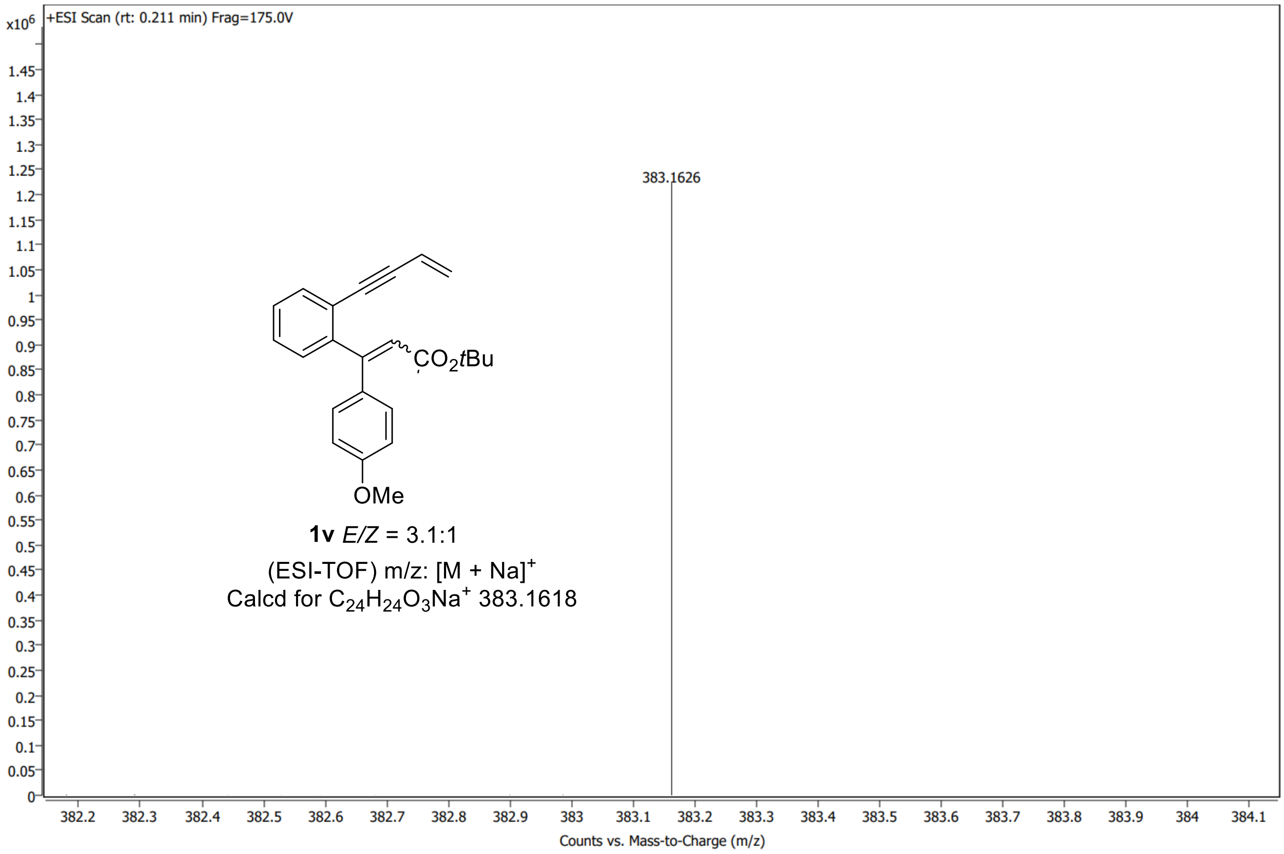
**1v** *E/Z* = 3.1:1

$^1$H NMR (400 MHz, CDCl$_3$)



**1v** *E/Z* = 3.1:1

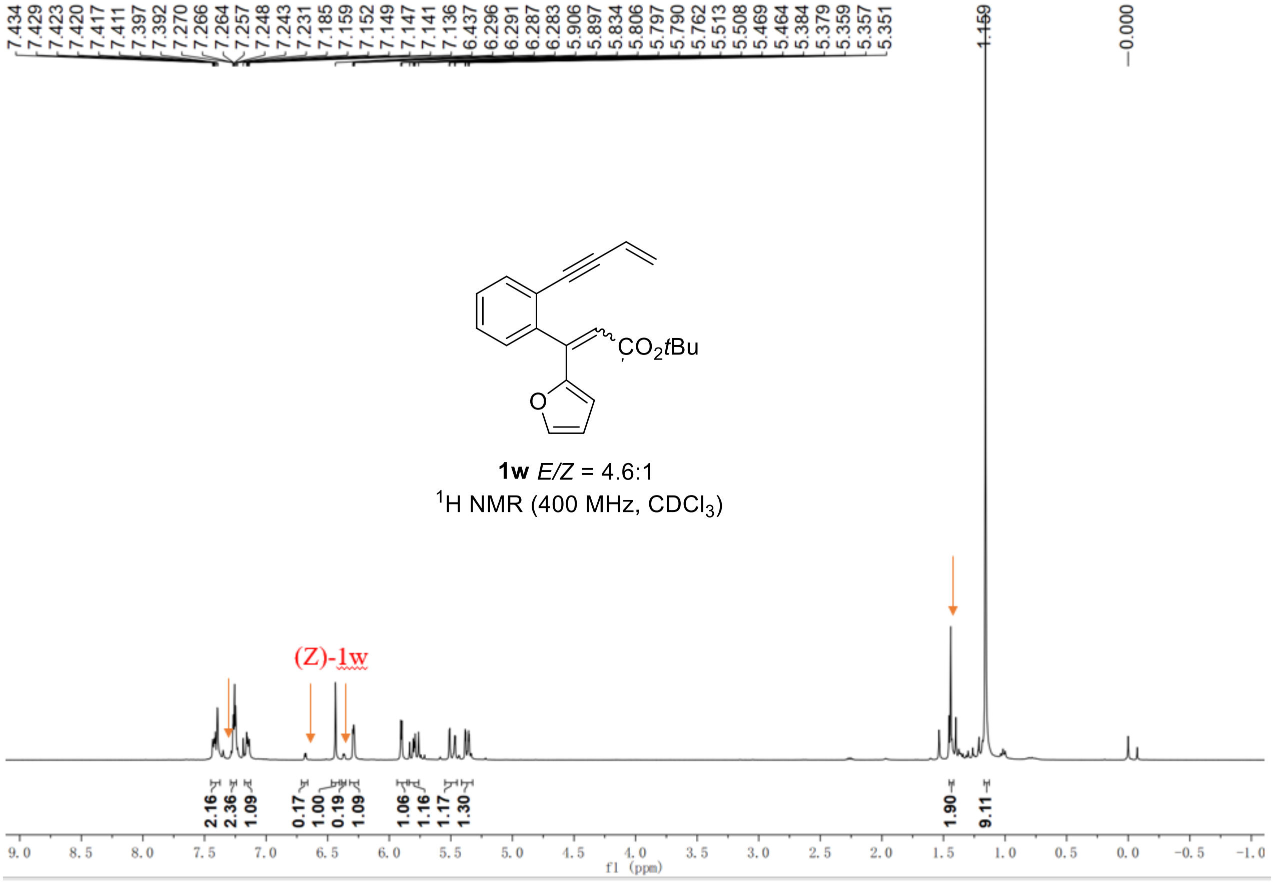
$^{13}$C NMR (150 MHz, CDCl$_3$)



**1v** *E/Z* = 3.1:1

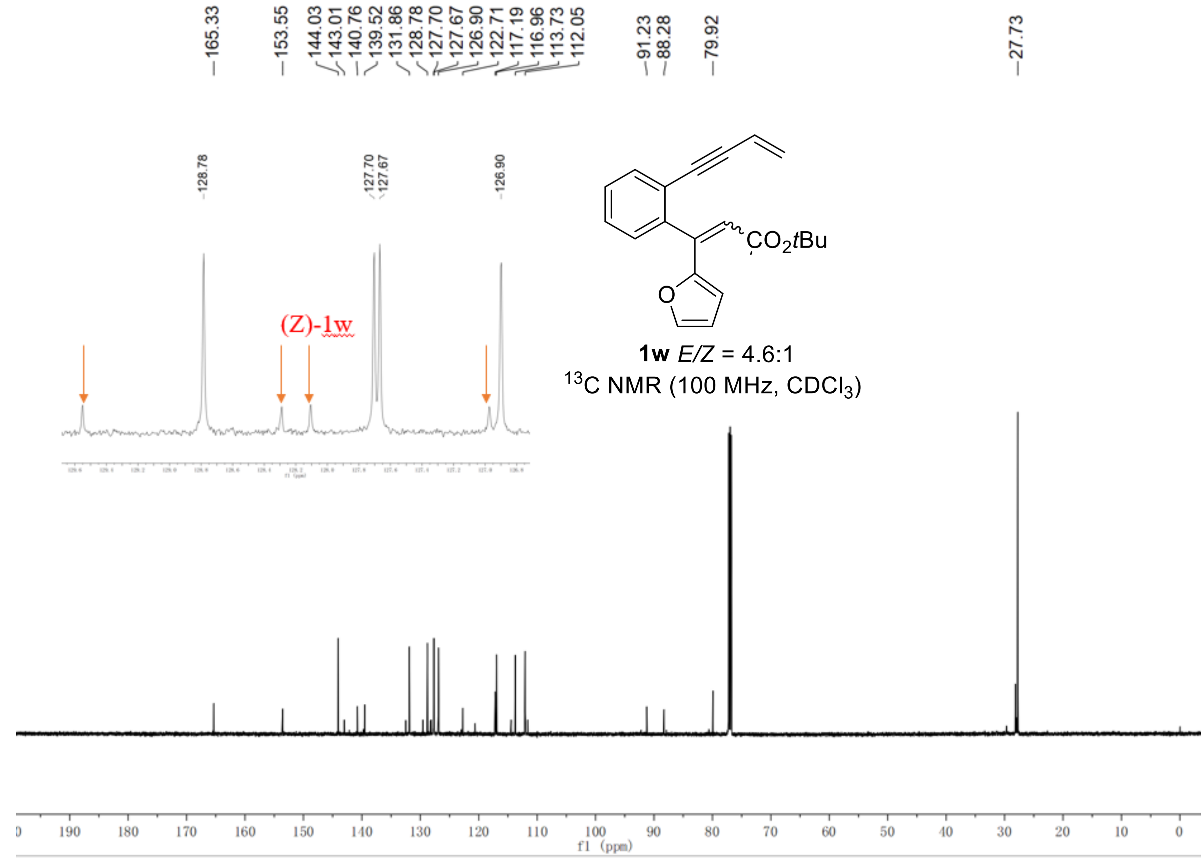
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{24}H_{24}O_3Na^+$ 383.1618



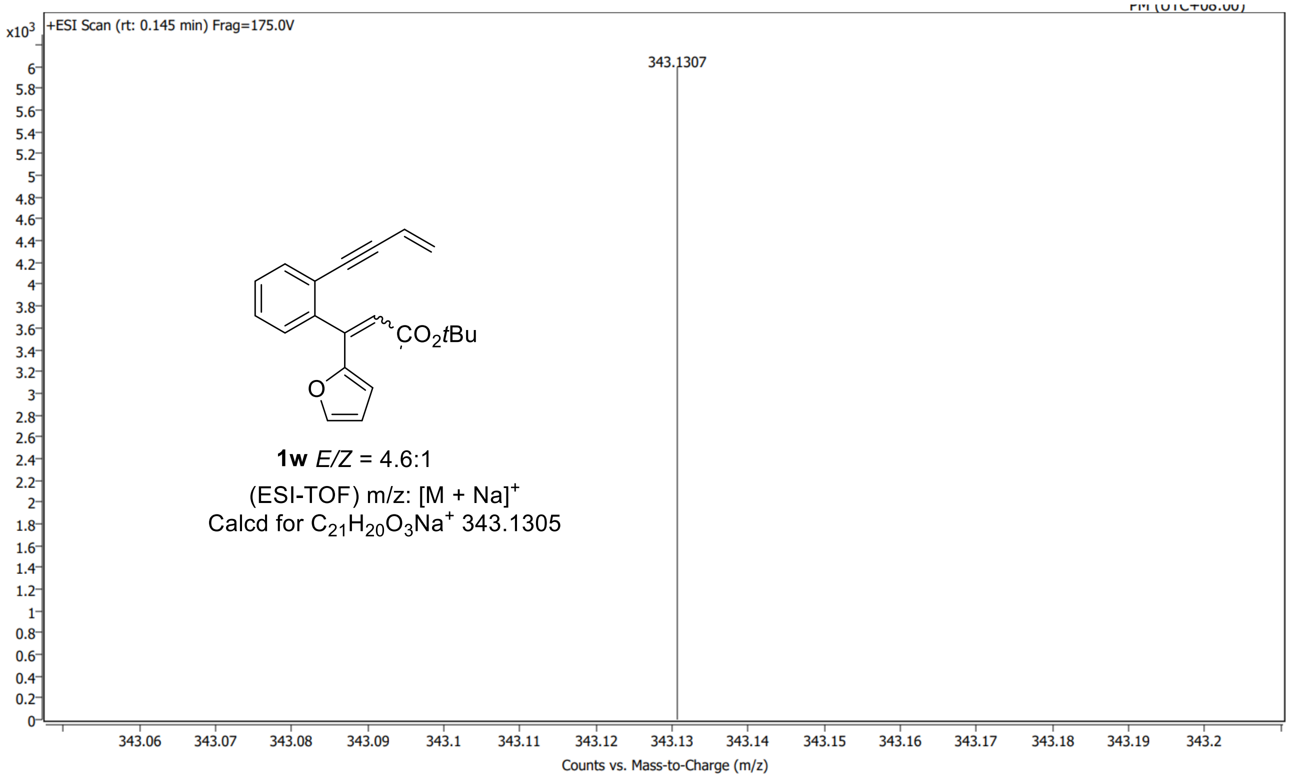
**1w** *E*/*Z* = 4.6:1

$^1$H NMR (400 MHz, $CDCl_3$)



**1w** *E*/*Z* = 4.6:1

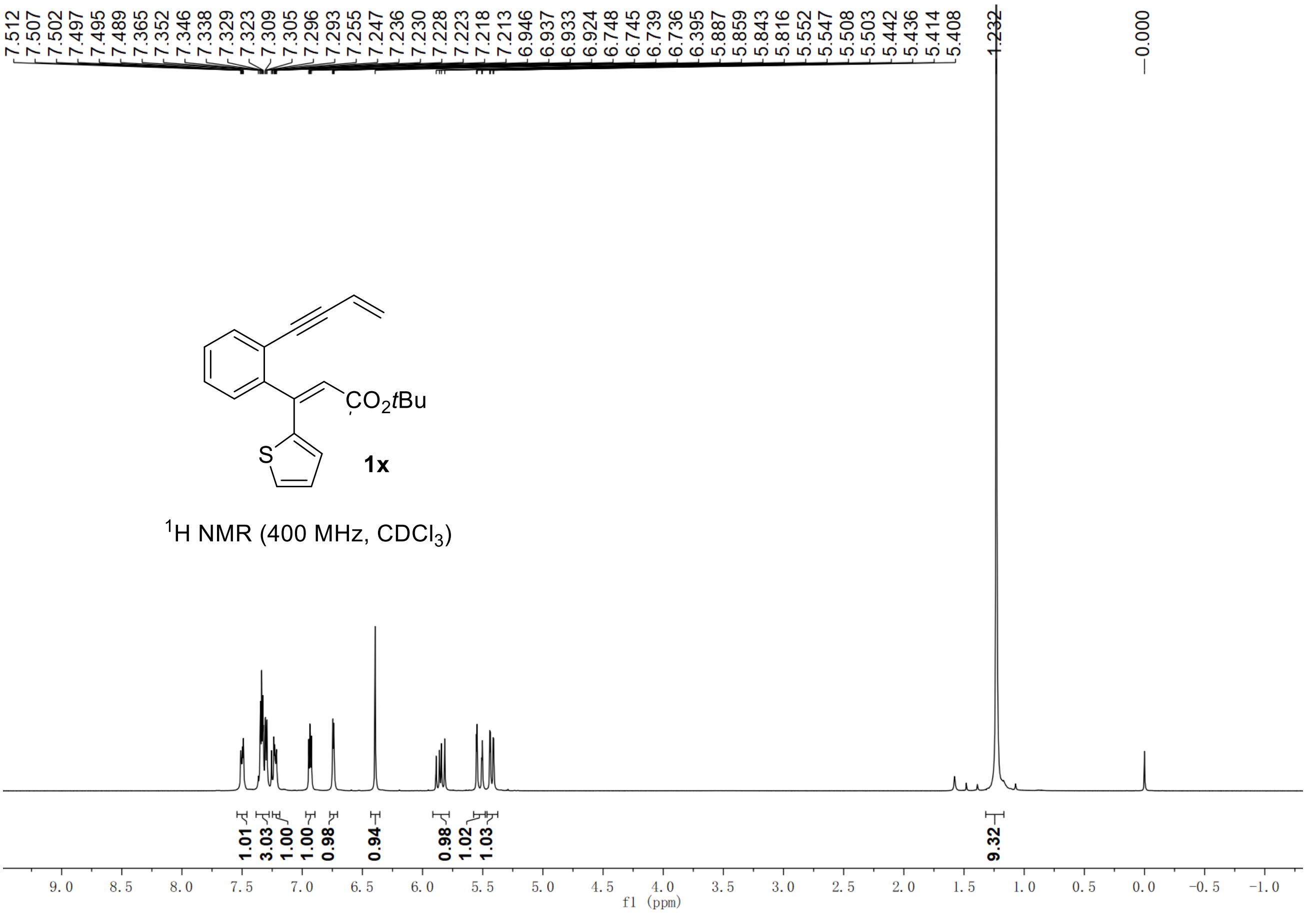
$^{13}$C NMR (100 MHz, $CDCl_3$)

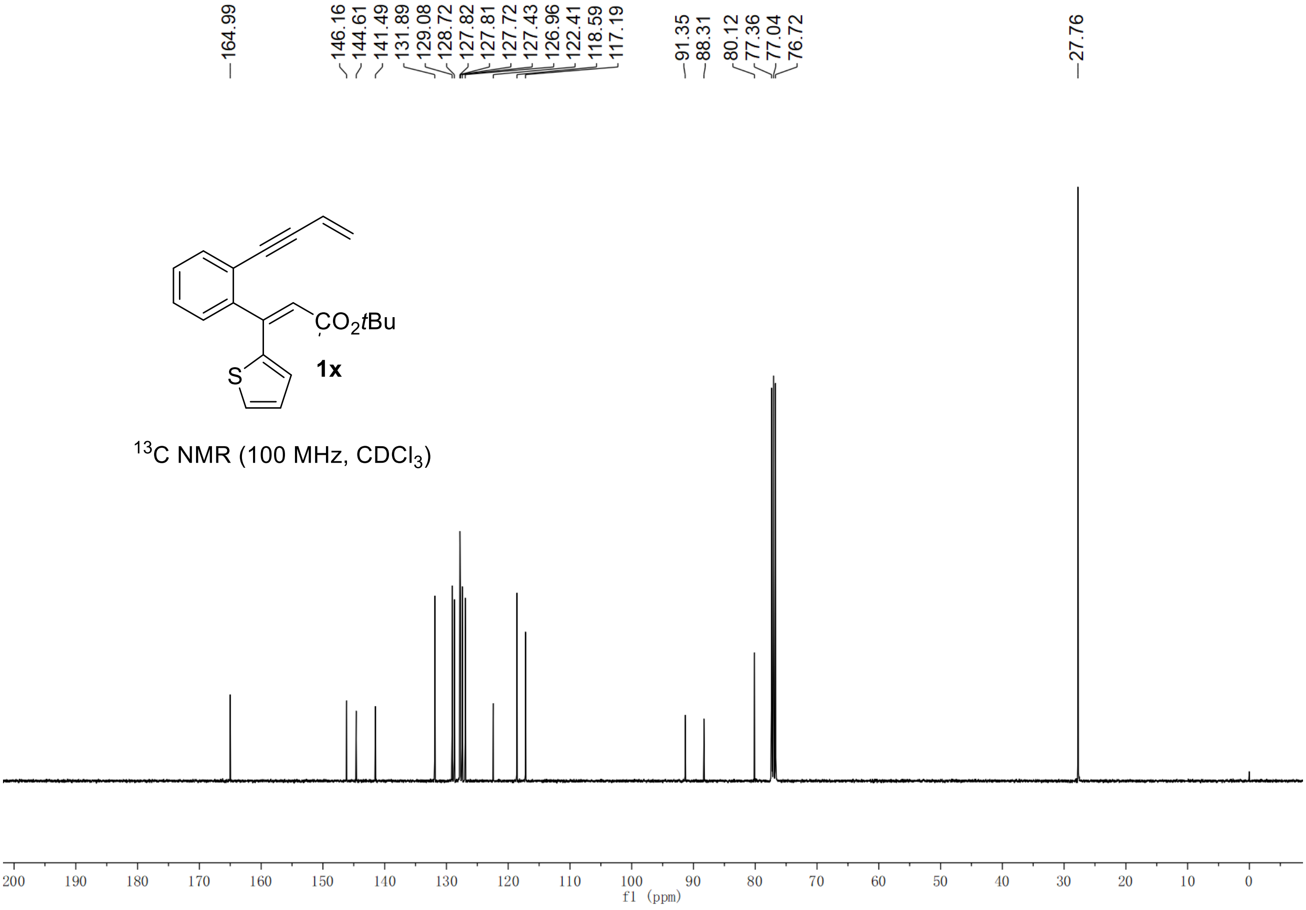


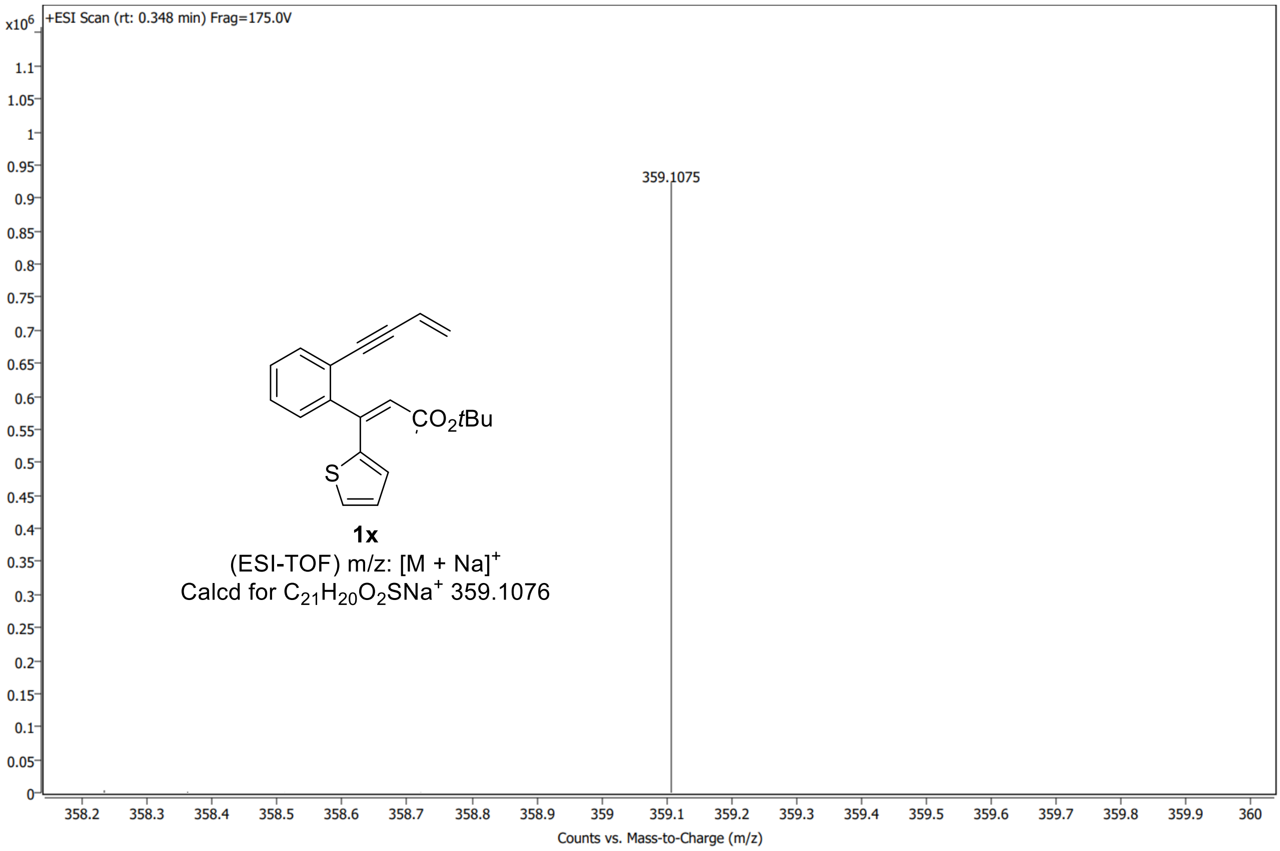
**1w** *E/Z* = 4.6:1

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{21}H_{20}O_3Na^+$ 343.1305


7.512
7.507
7.502
7.497
7.495
7.489
7.365
7.352
7.346
7.338
7.329
7.323
7.309
7.305
7.296
7.293
7.255
7.247
7.236
7.230
7.228
7.223
7.218
7.213
6.946
6.937
6.933
6.924
6.748
6.745
6.739
6.736
6.395
5.887
5.859
5.843
5.816
5.552
5.547
5.508
5.503
5.442
5.436
5.414
5.408
1.232
0.000
CO2tBu
S
1x
1H NMR (400 MHz, CDCl3)
1.01
3.03
1.00
1.00
0.98
0.94
0.98
1.02
1.03
9.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

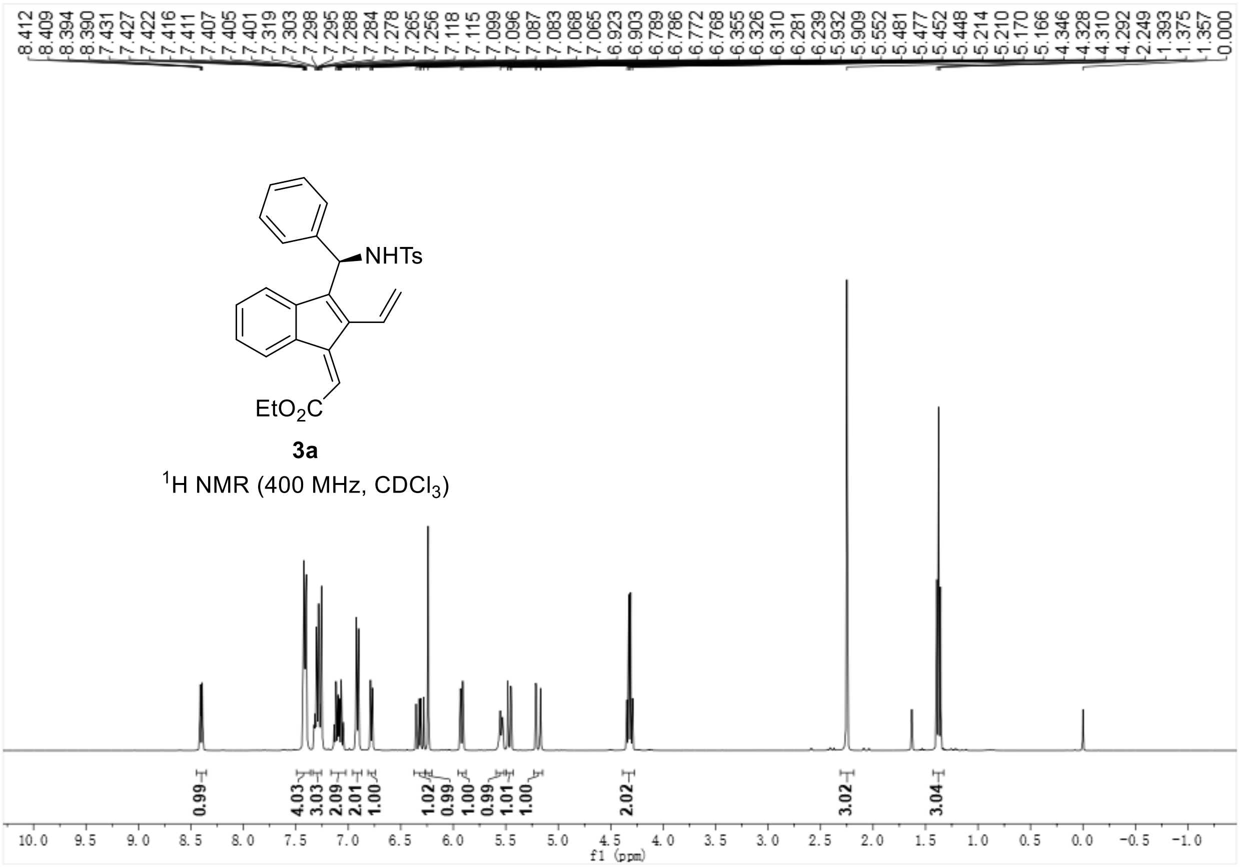

164.99
146.16
144.61
141.49
131.89
129.08
128.72
127.82
127.81
127.72
127.43
126.96
122.41
118.59
117.19
91.35
88.31
80.12
77.36
77.04
76.72
27.76
CO2tBu
S
1x
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**1x**

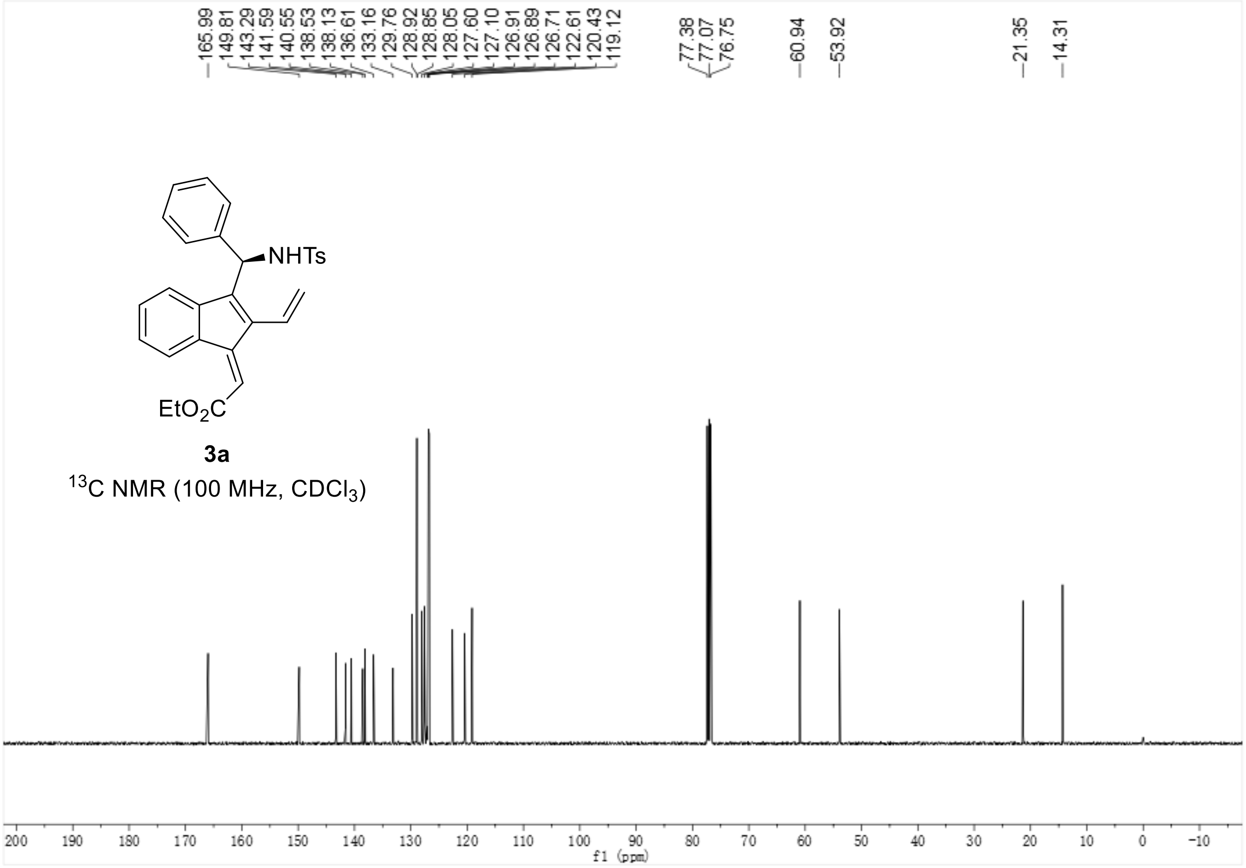
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{21}H_{20}O_2SNa^+$ 359.1076



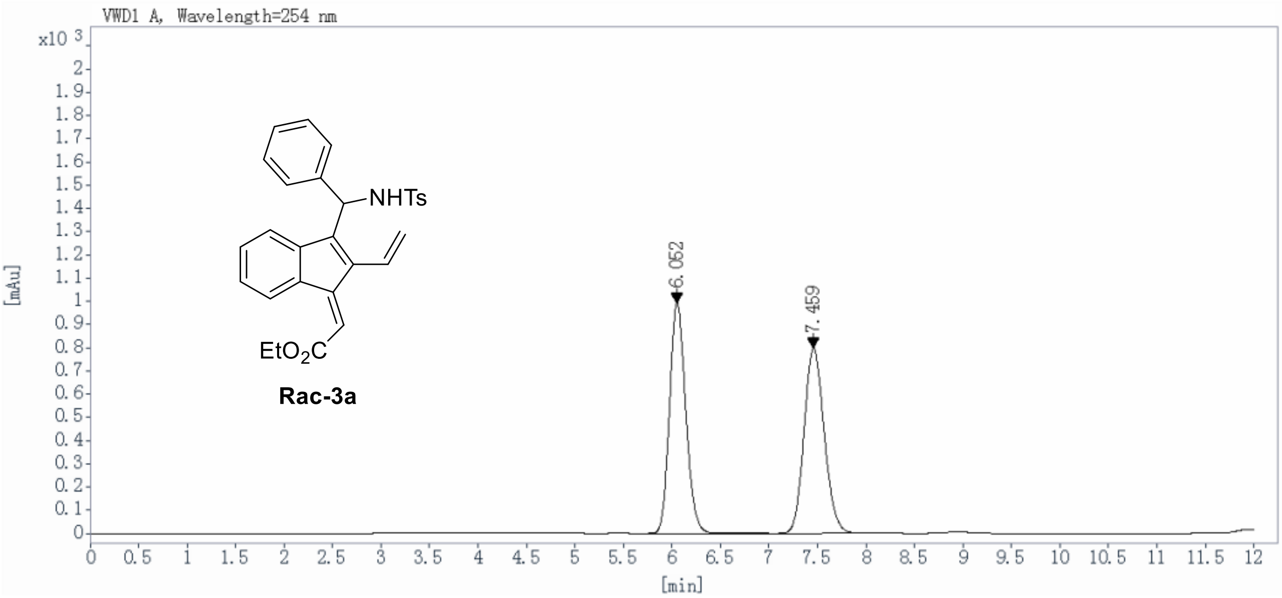
**3a**

$^1H$ NMR (400 MHz, $CDCl_3$)



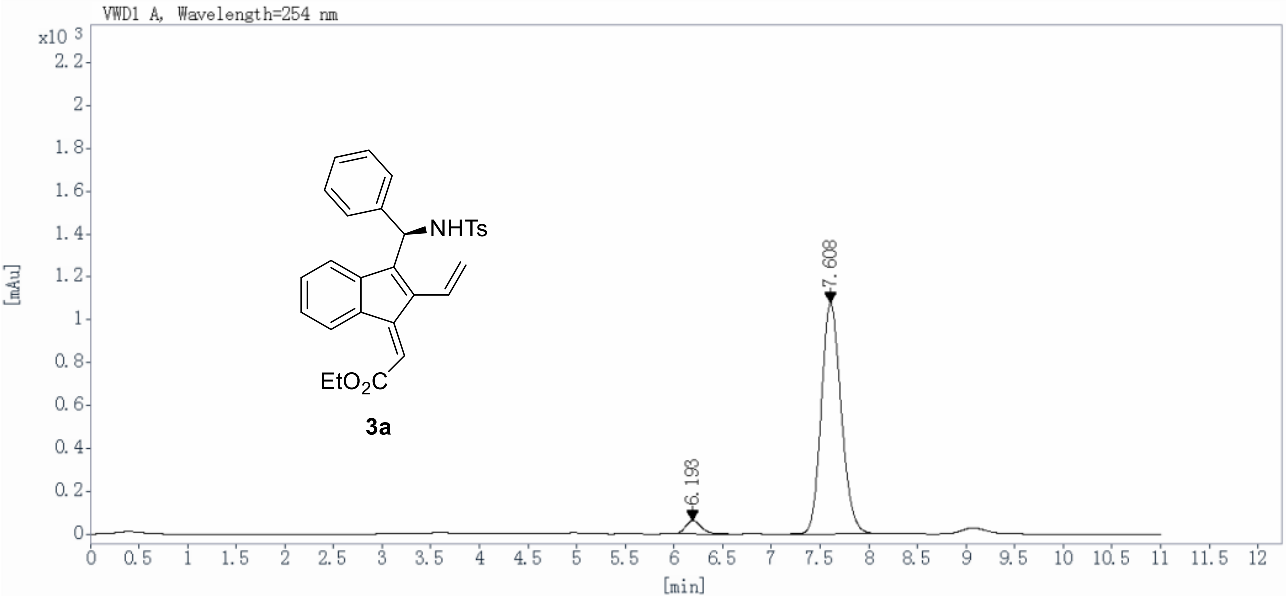
**3a**

$^{13}C$ NMR (100 MHz, $CDCl_3$)



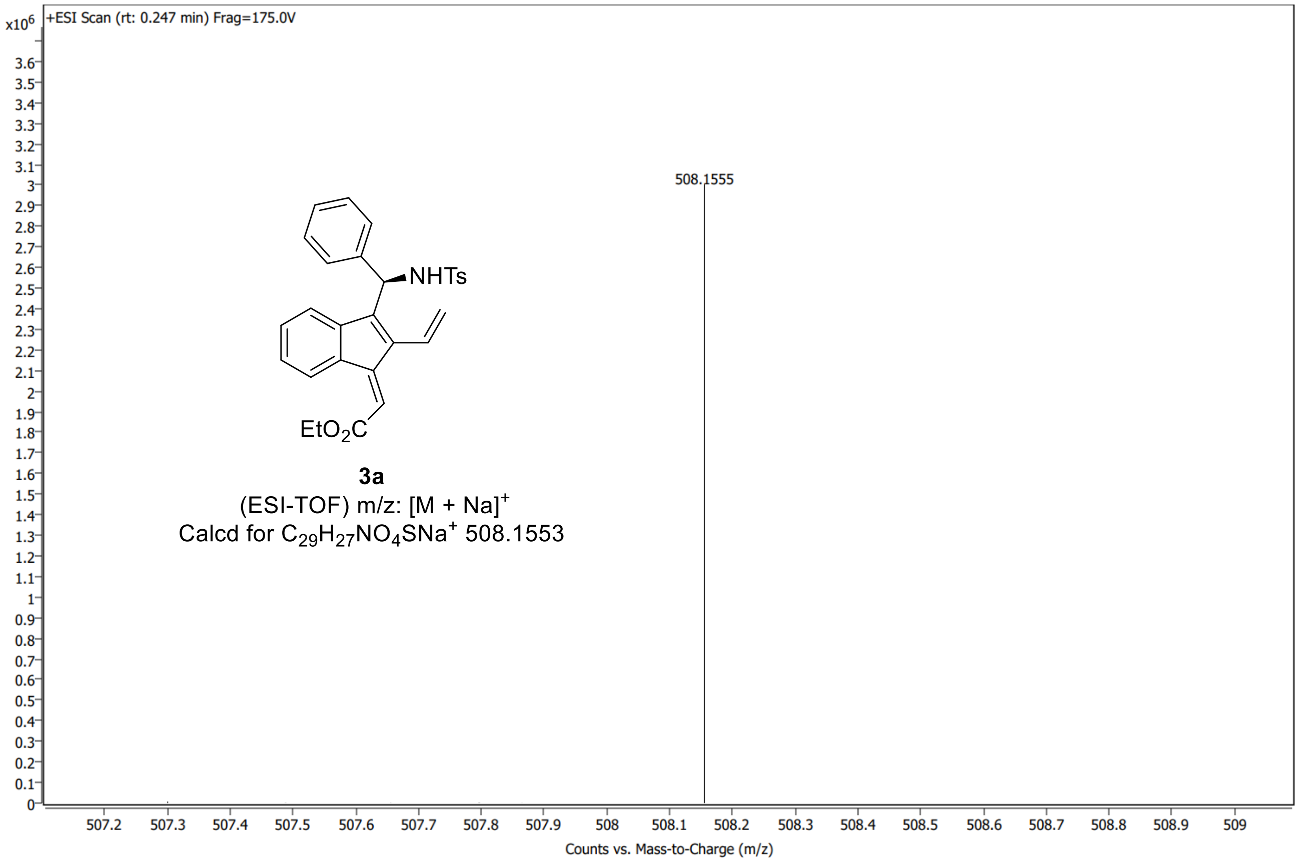
**Rac-3a**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.052 | BV R | 0.18 | 992.9355 | 11555.7979 | 49.9992 |
| 7.459 | BB | 0.23 | 797.1862 | 11556.1553 | 50.0008 |
| | | | Totals: | 23111.9531 | 100.0000 |



**3a**

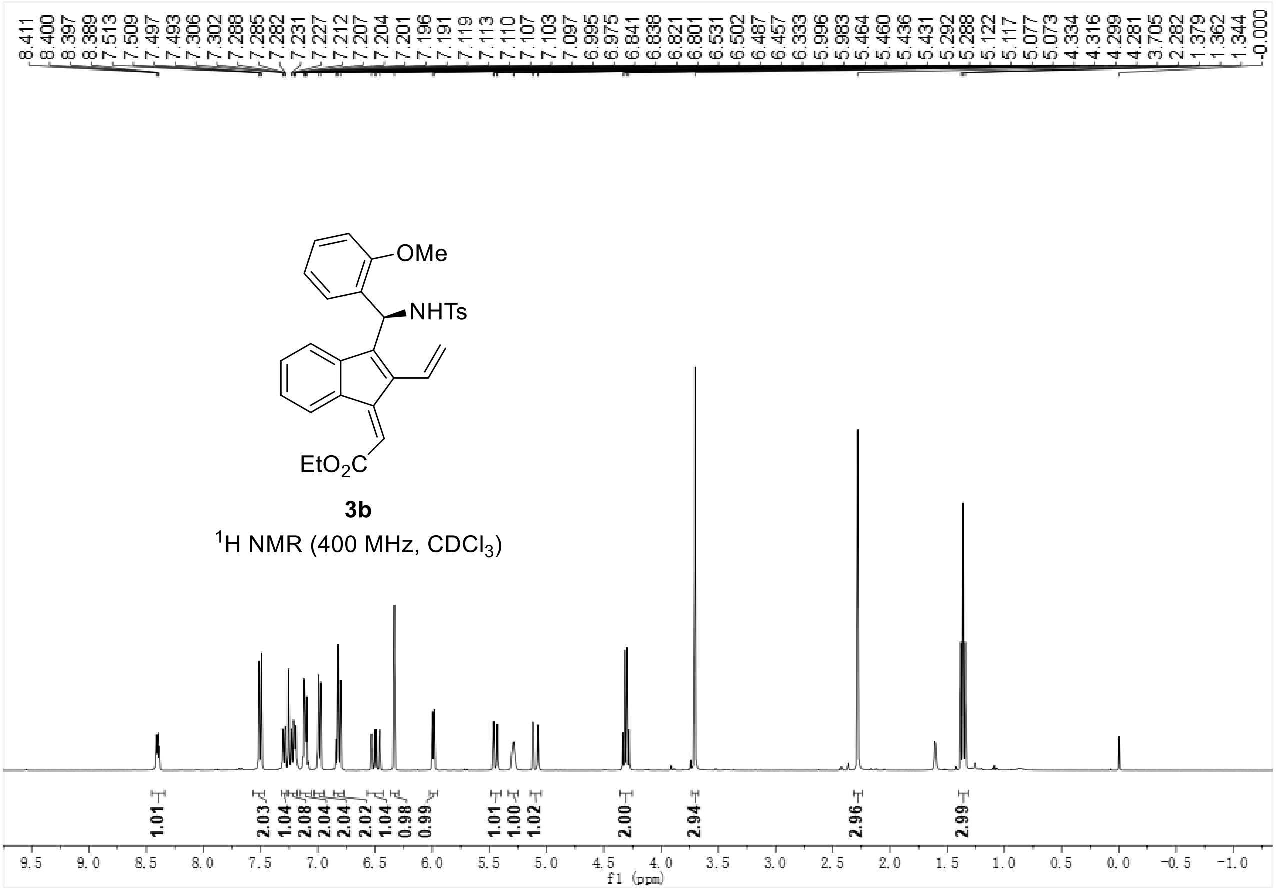
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.193 | BBA | 0.17 | 62.2099 | 694.1777 | 4.3245 |
| 7.608 | BBA | 0.22 | 1080.3180 | 15358.0850 | 95.6755 |
| | | | Totals: | 16052.2627 | 100.0000 |



**3a**

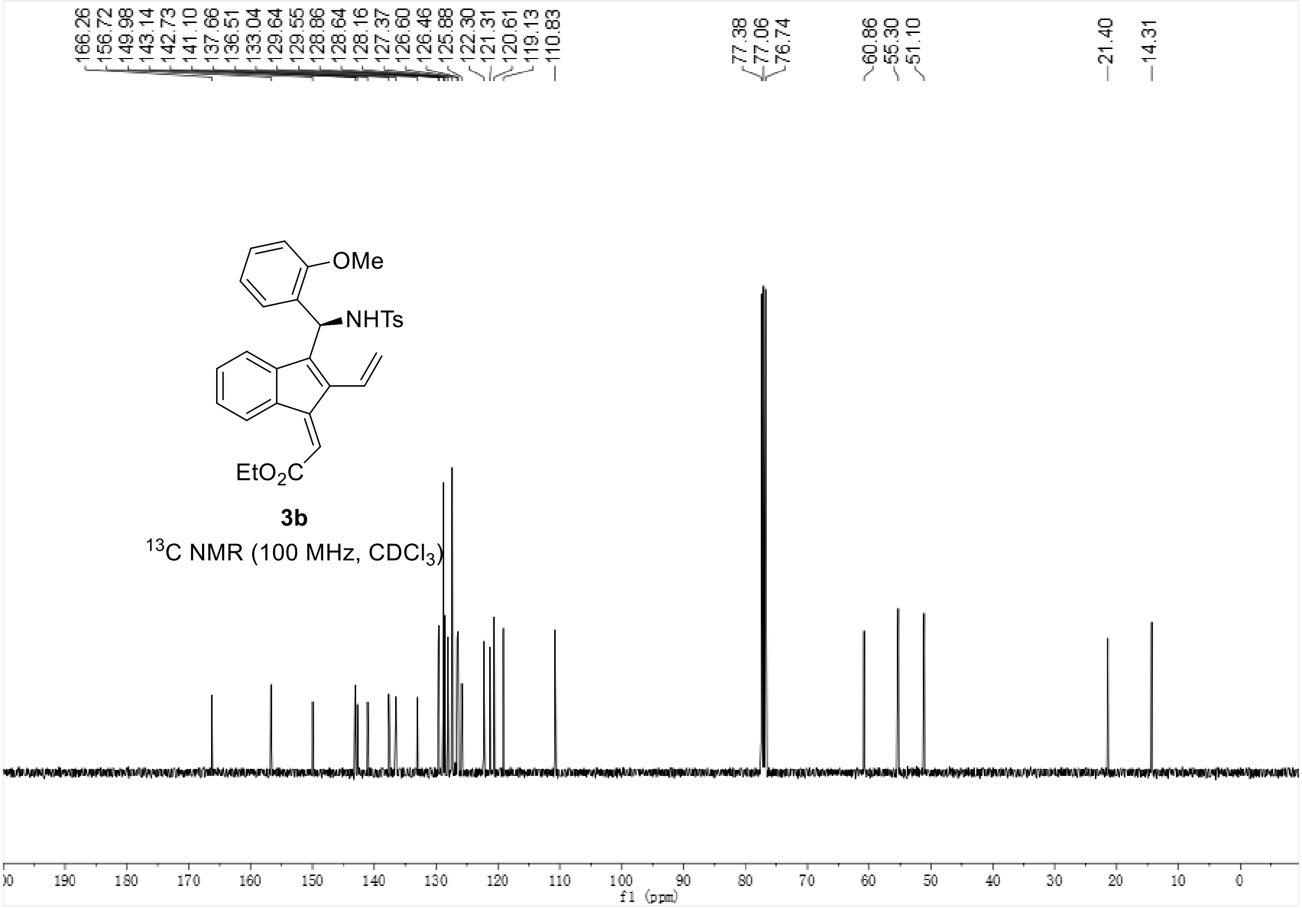
(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{29}H_{27}NO_4SNa^+$ 508.1553



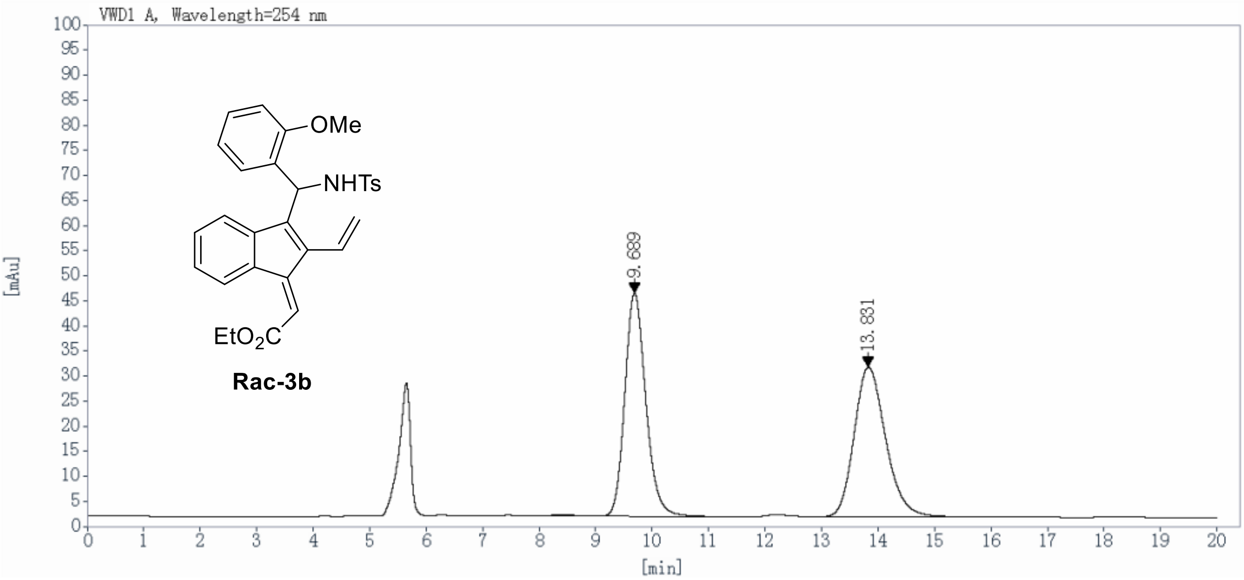
**3b**

$^{1}$H NMR (400 MHz, $CDCl_3$)

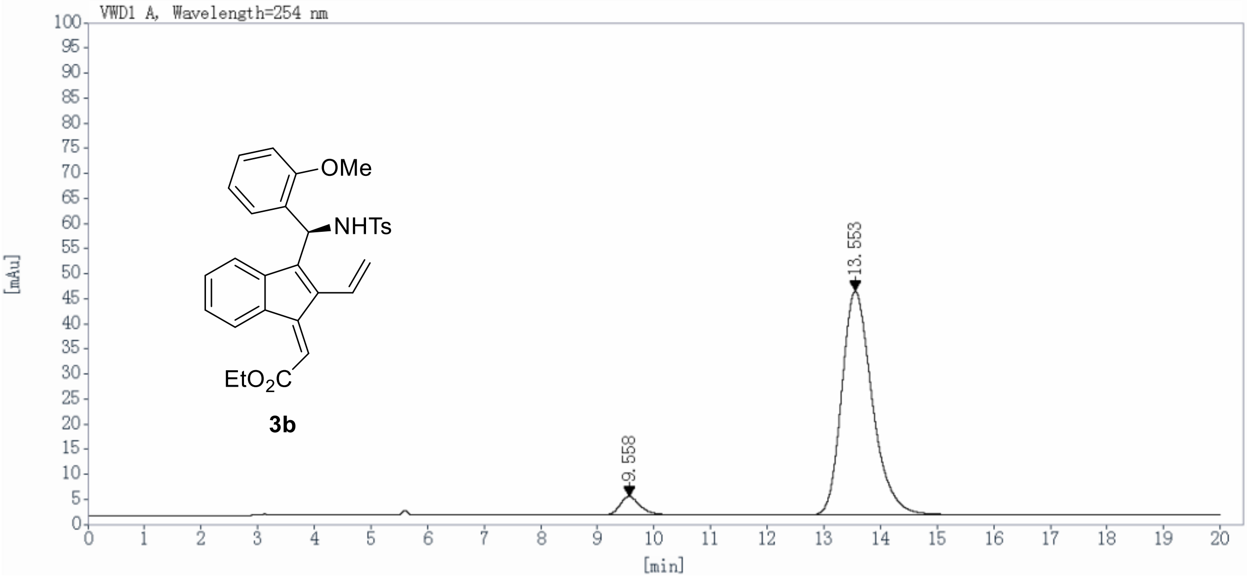


**3b**

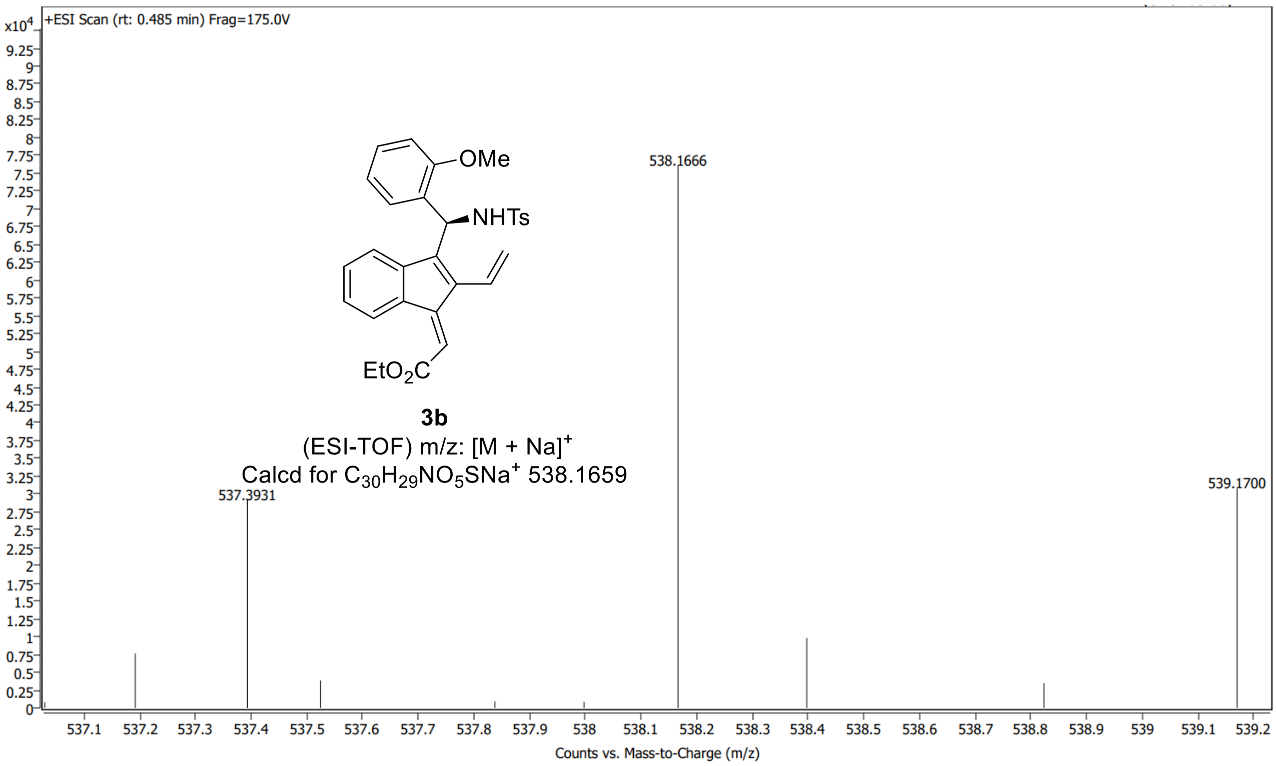
$^{13}$C NMR (100 MHz, $CDCl_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.689 | VB R | 0.40 | 312.5956 | 8160.5161 | 50.2187 |
| 13.831 | BB | 0.59 | 209.3700 | 8089.4248 | 49.7813 |
| | | | Totals: | 16249.9409 | 100.0000 |



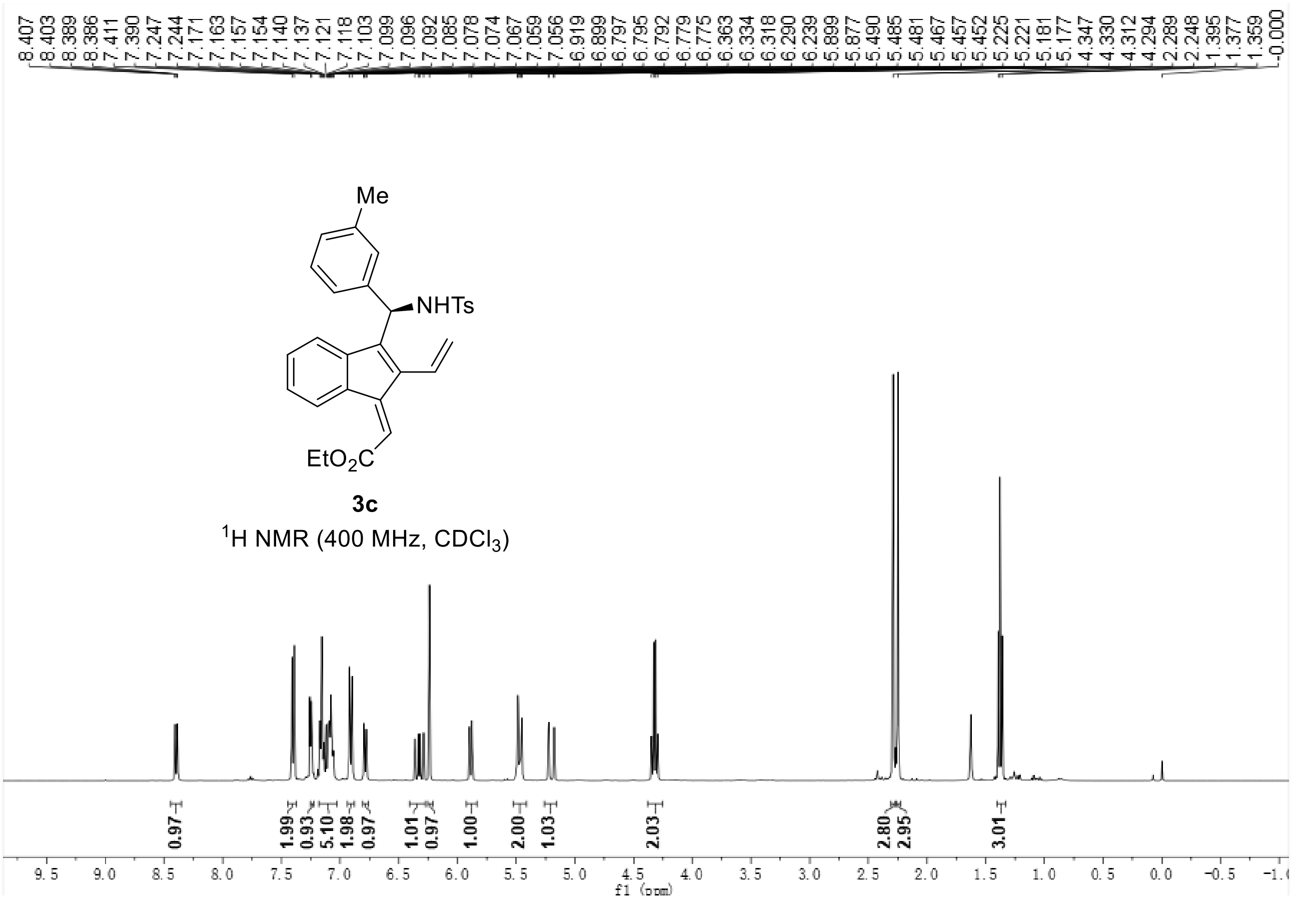
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.558 | BBA | 0.37 | 42.5479 | 1031.7642 | 5.0256 |
| 13.553 | BB | 0.57 | 519.6494 | 19498.4609 | 94.9744 |
| | | | Totals: | 20530.2251 | 100.0000 |



**3b**

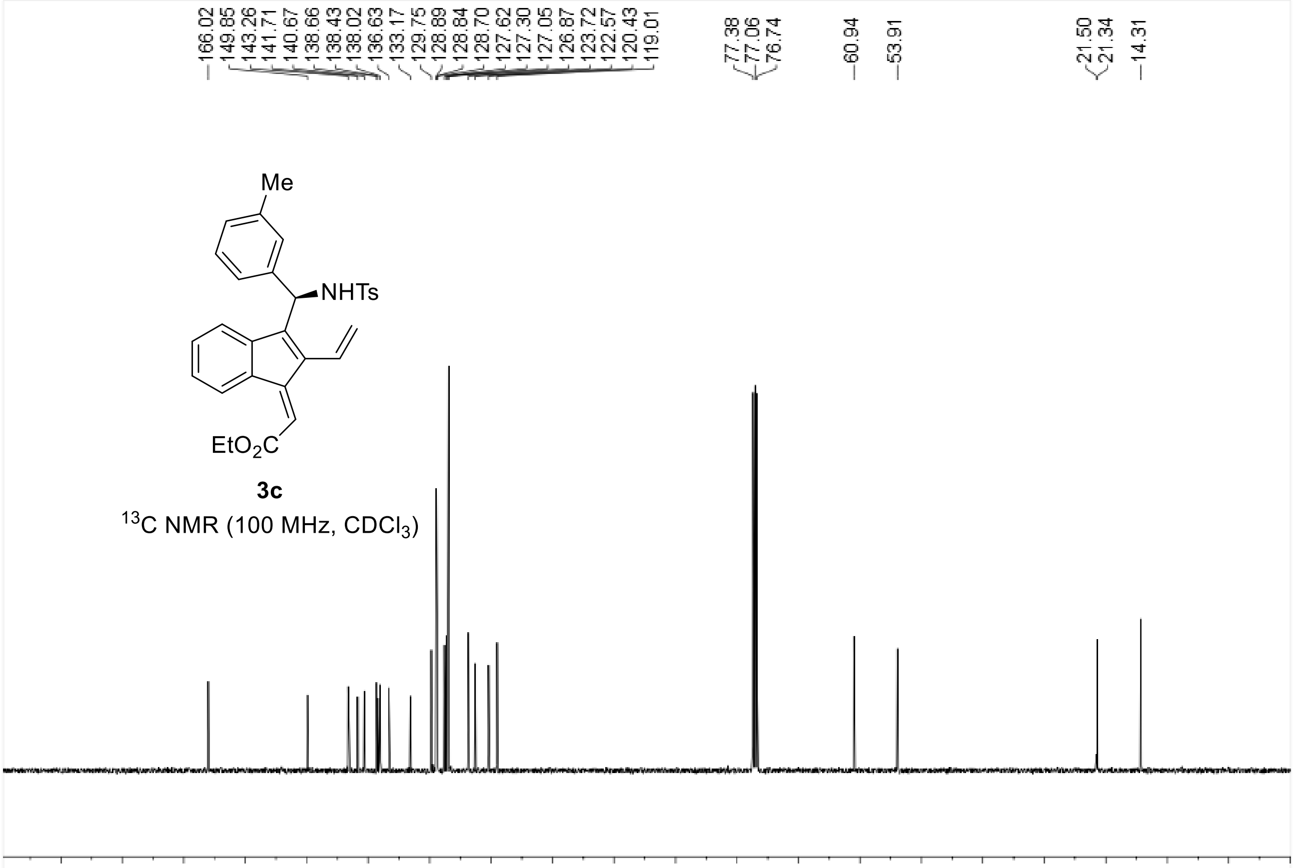
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{29}NO_5SNa^+$ 538.1659



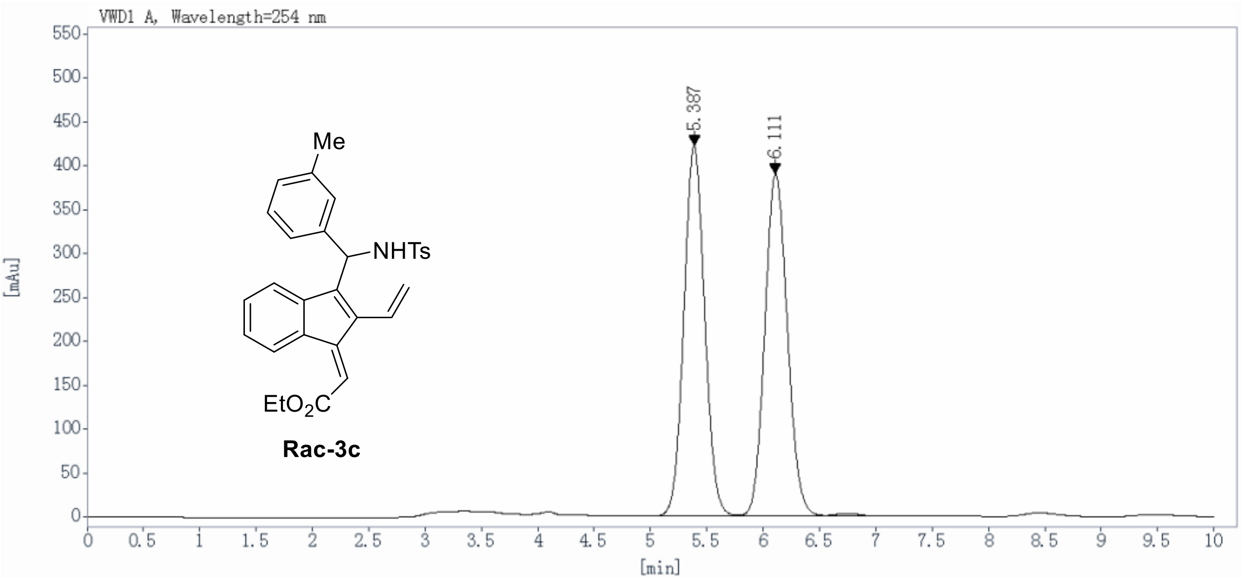
**3c**

$^1$H NMR (400 MHz, $CDCl_3$)



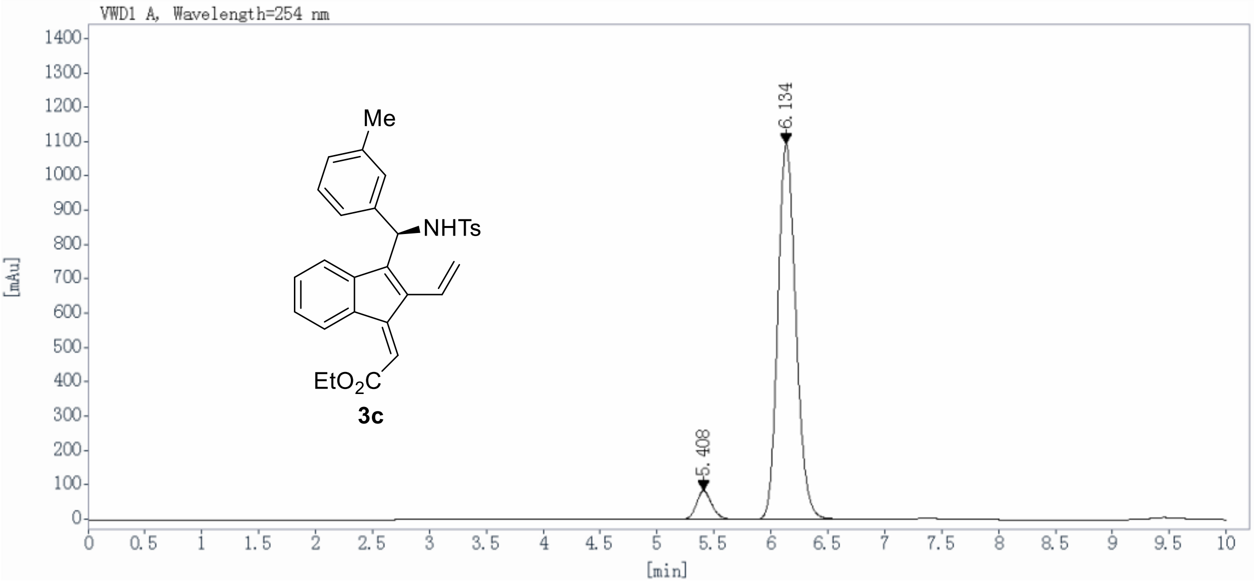
**3c**

$^{13}$C NMR (100 MHz, $CDCl_3$)



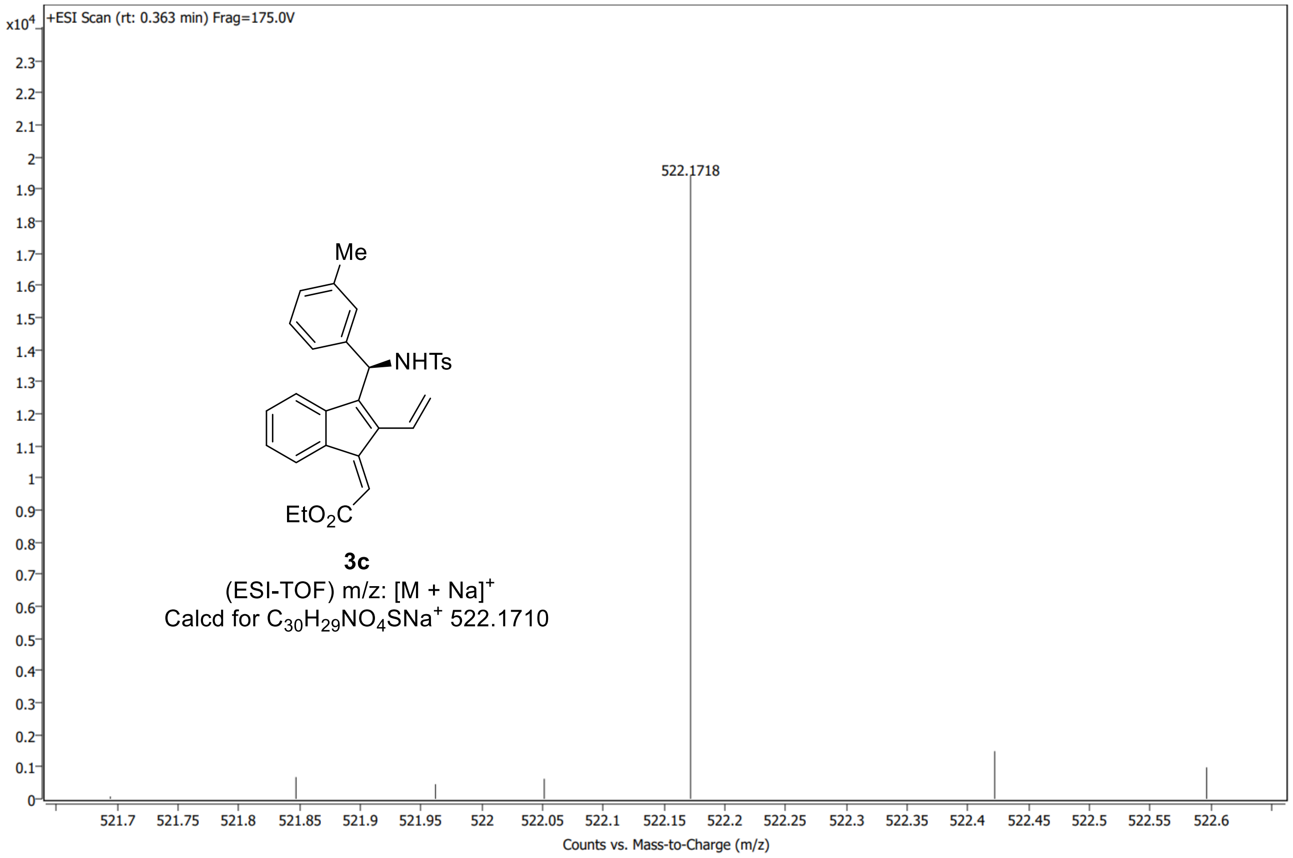
**Rac-3c**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.387 | BV | 0.20 | 422.4815 | 5417.5923 | 49.6468 |
| 6.111 | VV R | 0.22 | 390.1780 | 5494.6670 | 50.3532 |
| | | | Totals: | 10912.2593 | 100.0000 |



**3c**

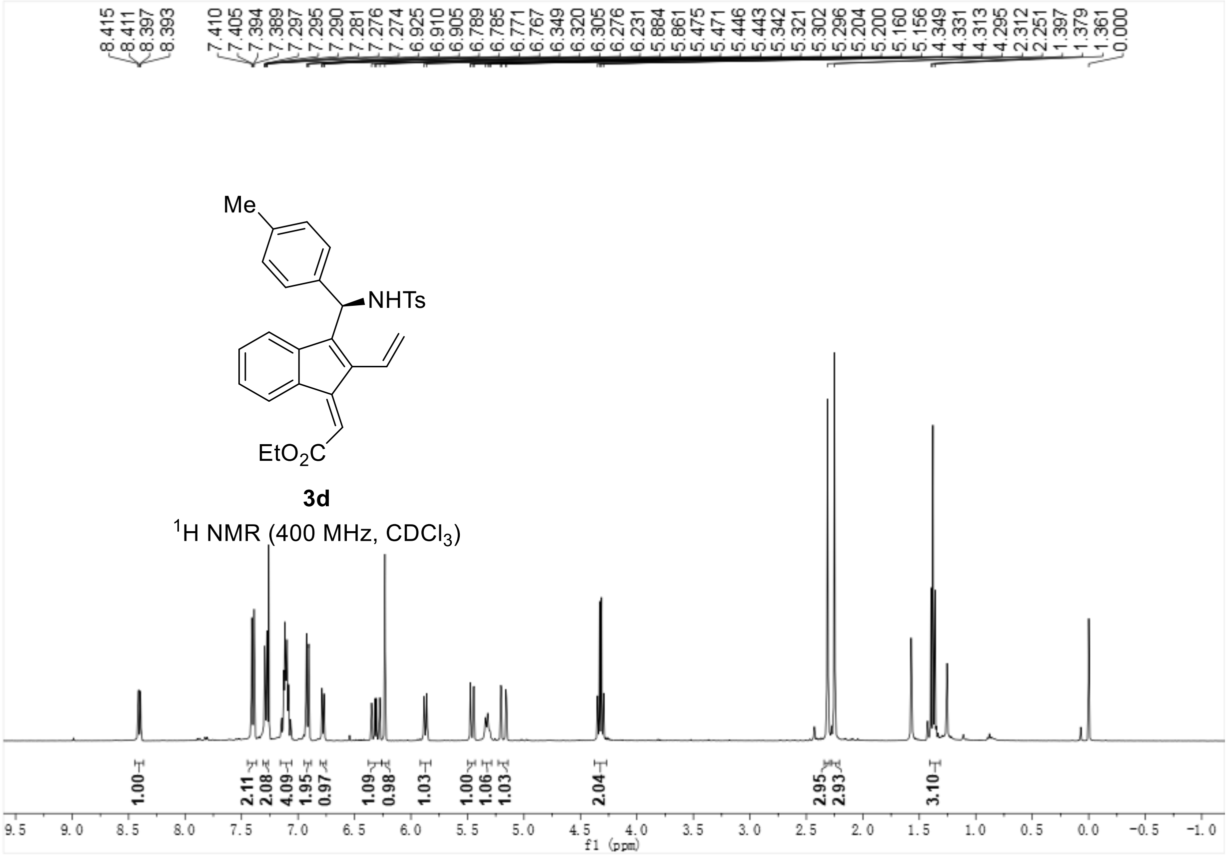
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.408 | BB | 0.15 | 83.2879 | 792.8492 | 6.1230 |
| 6.134 | BV R | 0.17 | 1093.6282 | 12155.8057 | 93.8770 |
| | | | Totals: | 12948.6548 | 100.0000 |



**3c**

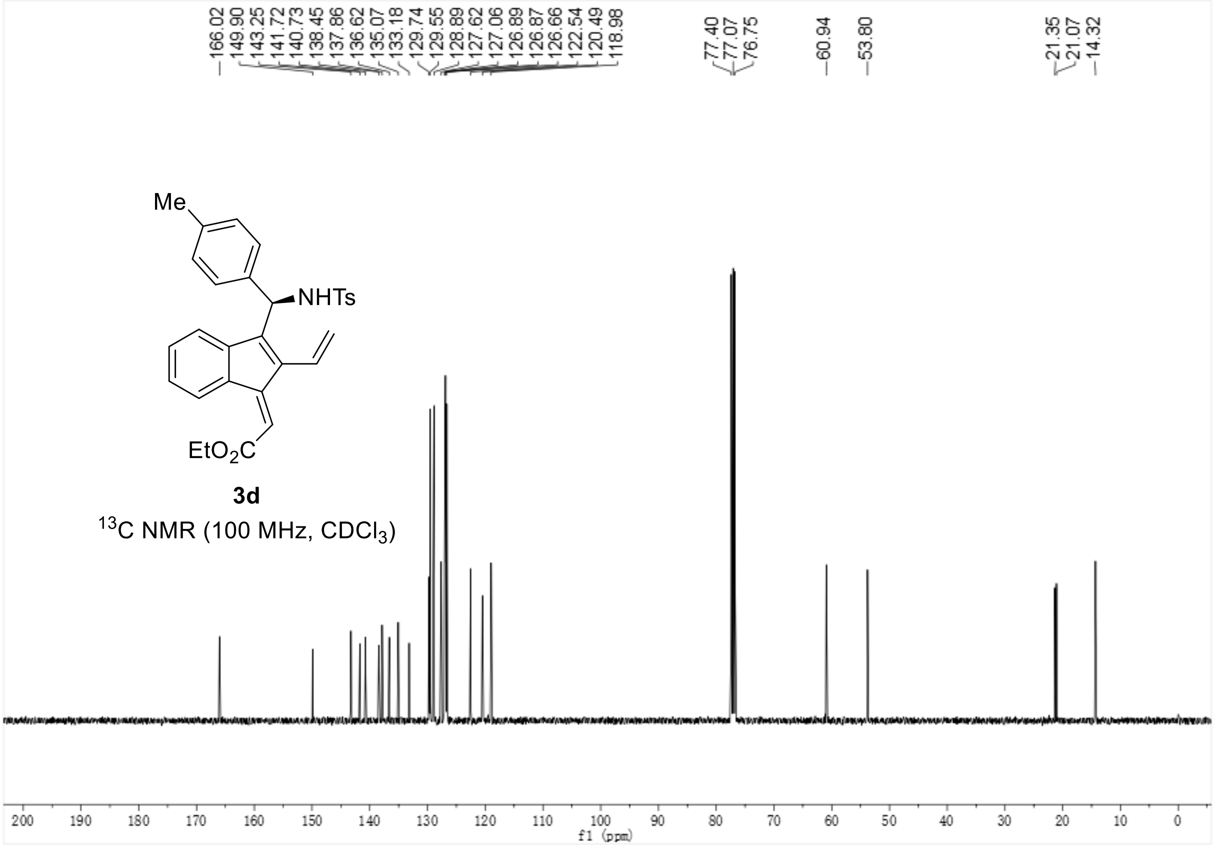
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710



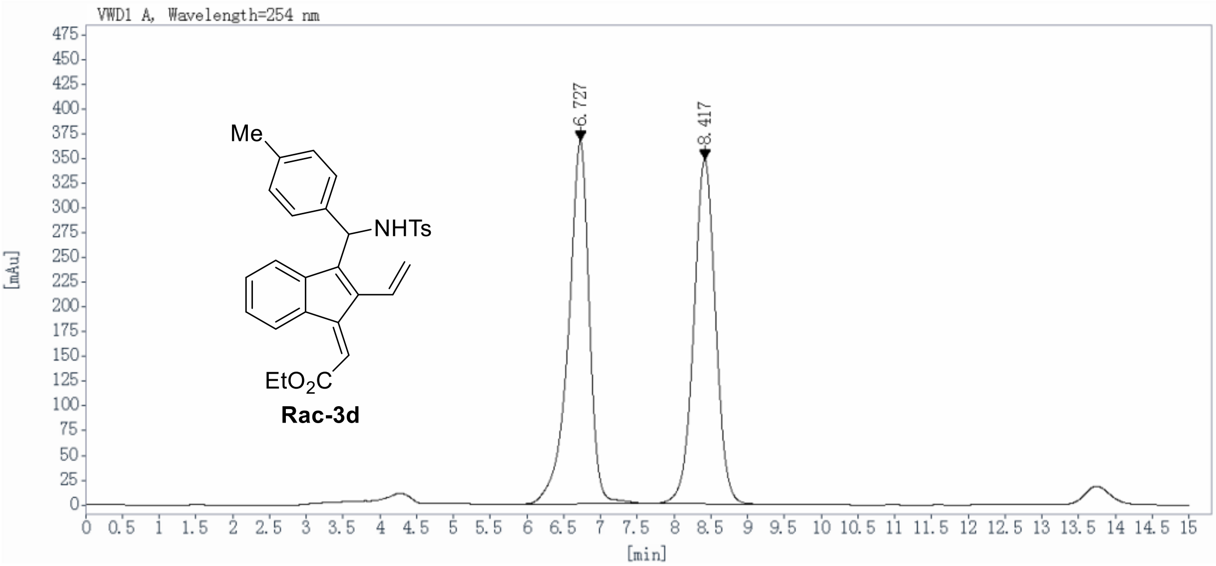
**3d**

$^1$H NMR (400 MHz, CDCl$_3$)



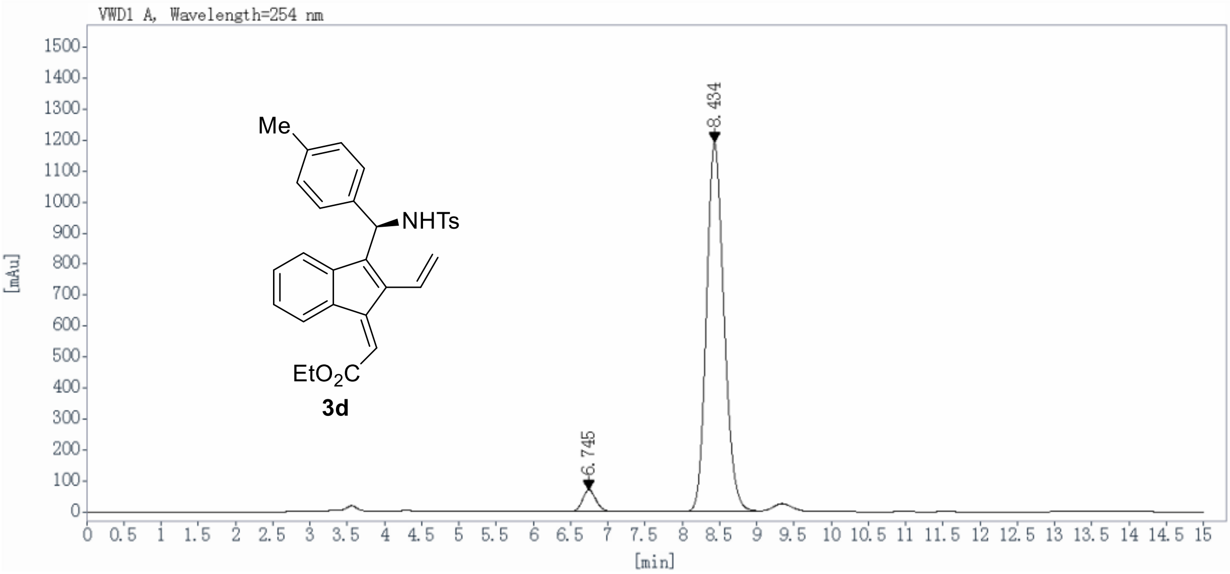
**3d**

$^{13}$C NMR (100 MHz, CDCl$_3$)



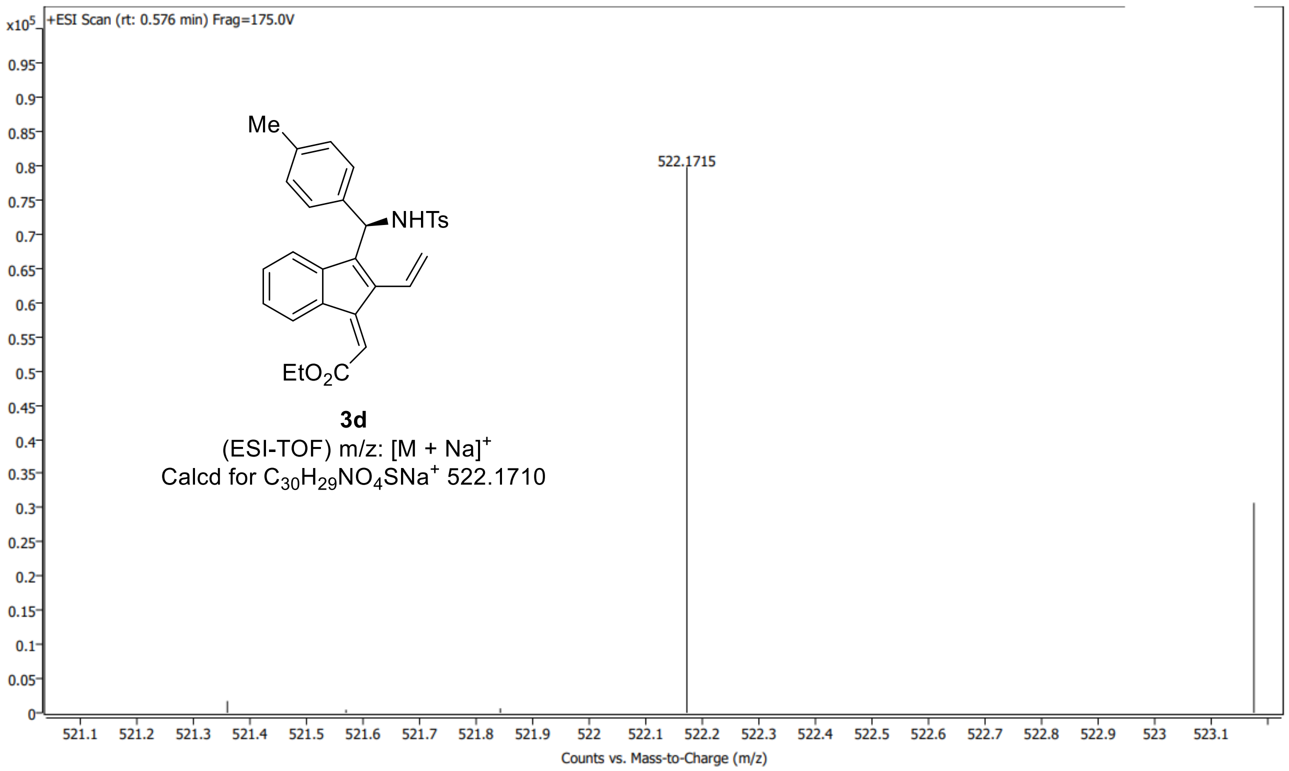
**Rac-3d**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.727 | BB | 0.29 | 366.7161 | 7245.6138 | 50.3393 |
| 8.417 | BB | 0.32 | 348.1396 | 7147.9292 | 49.6607 |
| | | | Totals: | 14393.5430 | 100.0000 |



**3d**

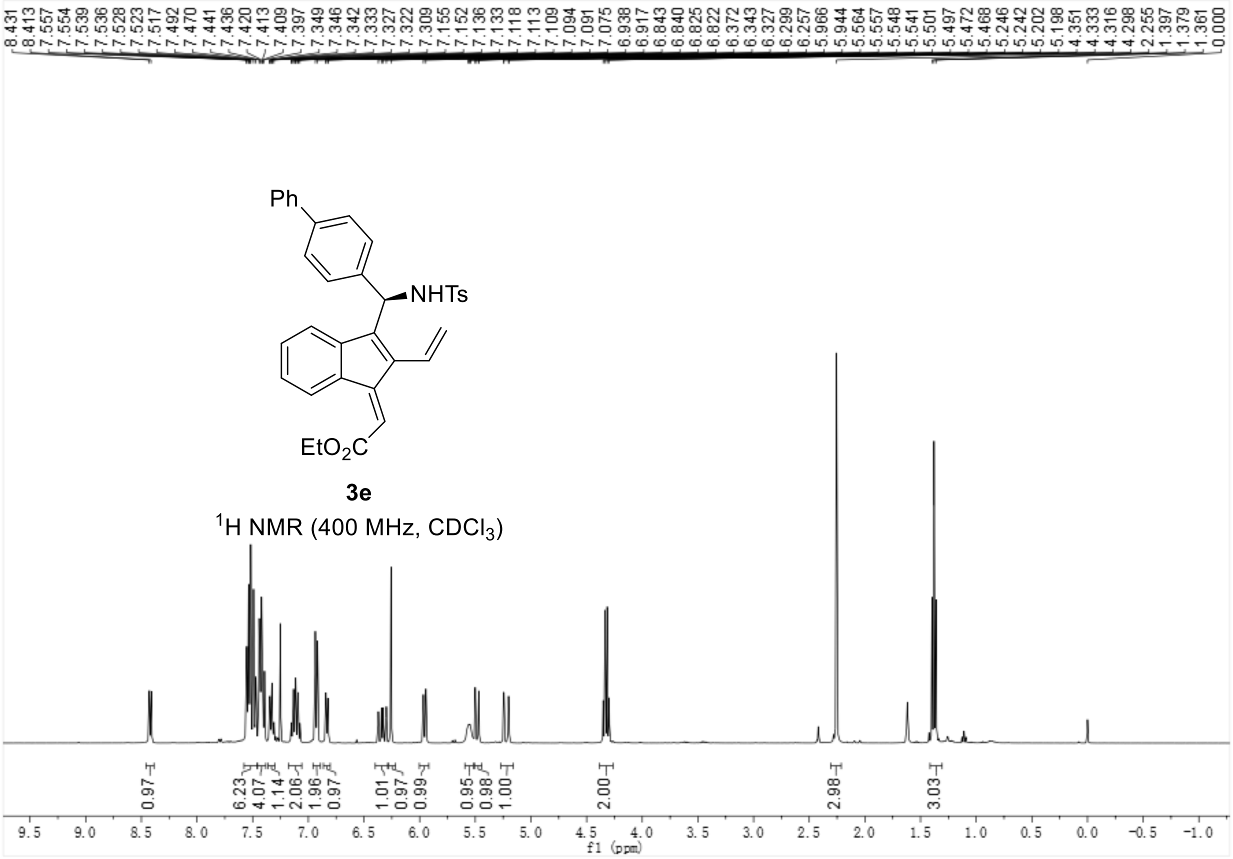
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.745 | BB | 0.19 | 70.1946 | 880.4067 | 4.3040 |
| 8.434 | BB | 0.25 | 1190.4943 | 19575.2656 | 95.6960 |
| | | | Totals: | 20455.6724 | 100.0000 |



**3d**

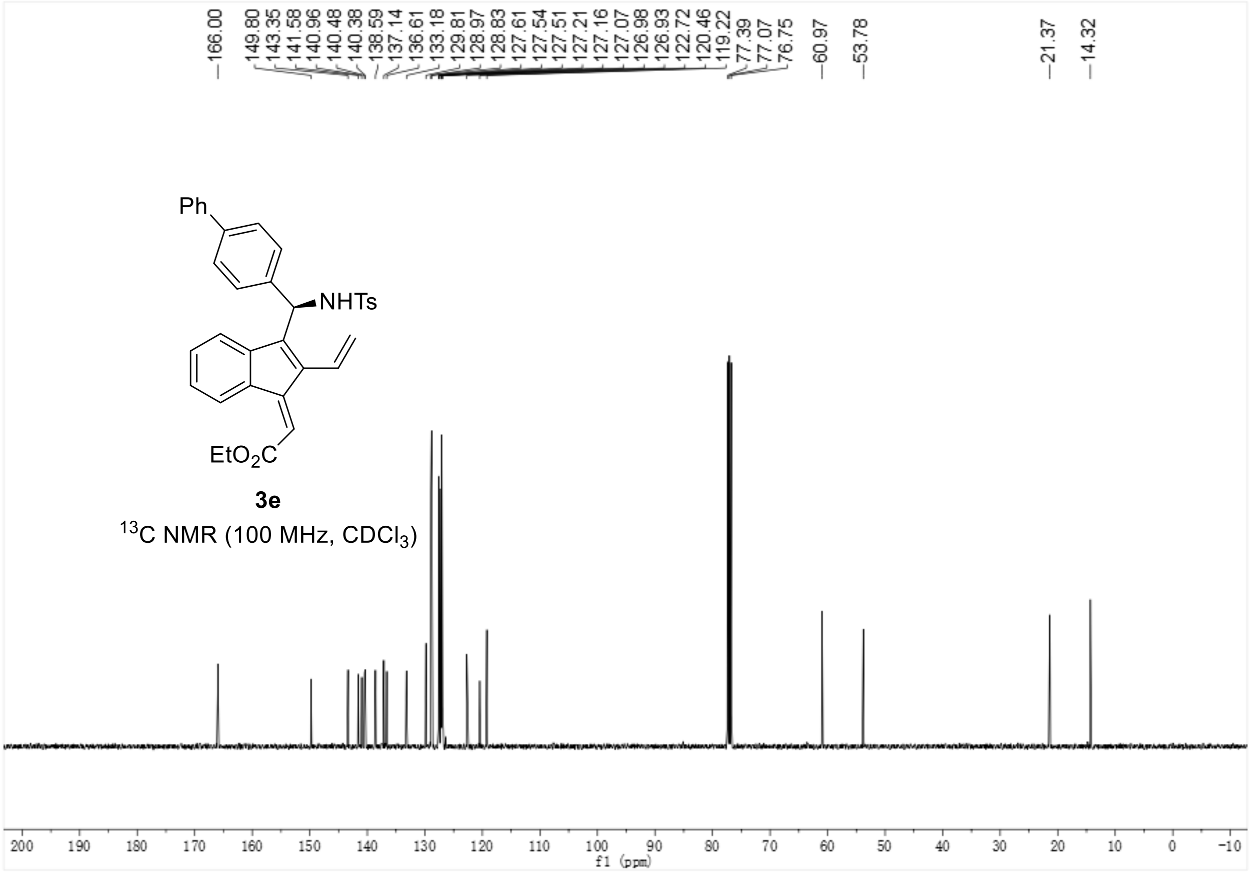
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710



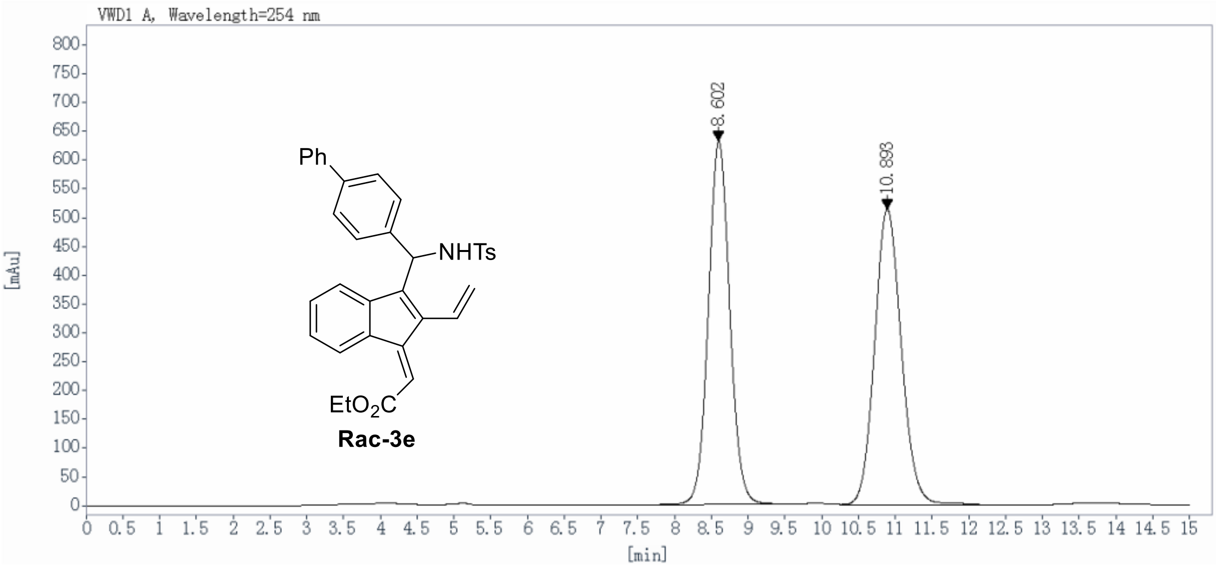
**3e**

$^1$H NMR (400 MHz, CDCl$_3$)

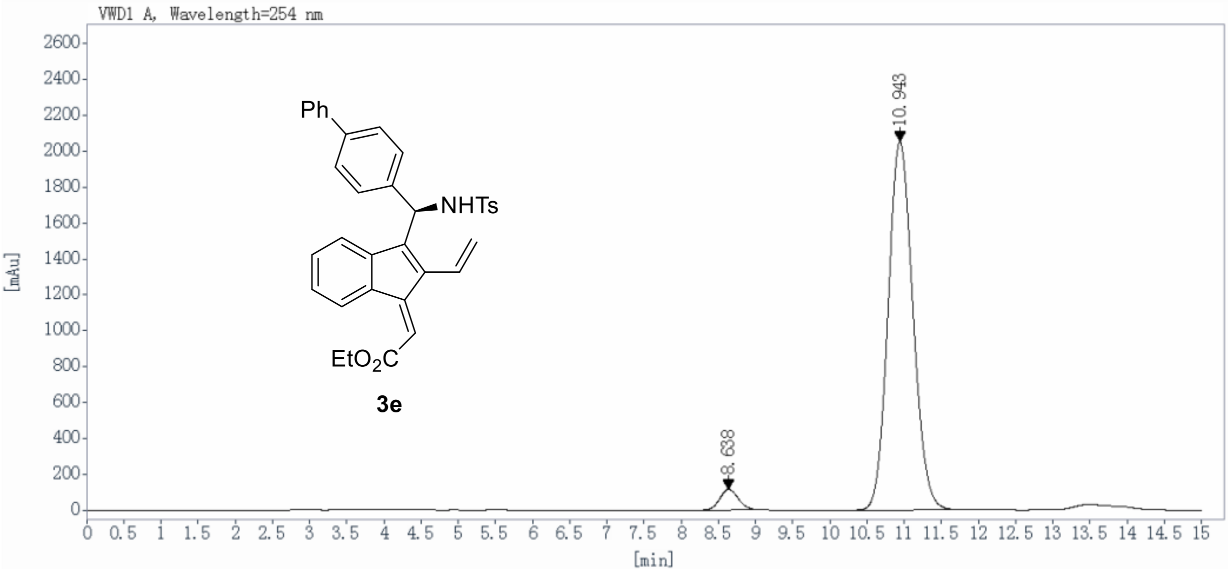


**3e**

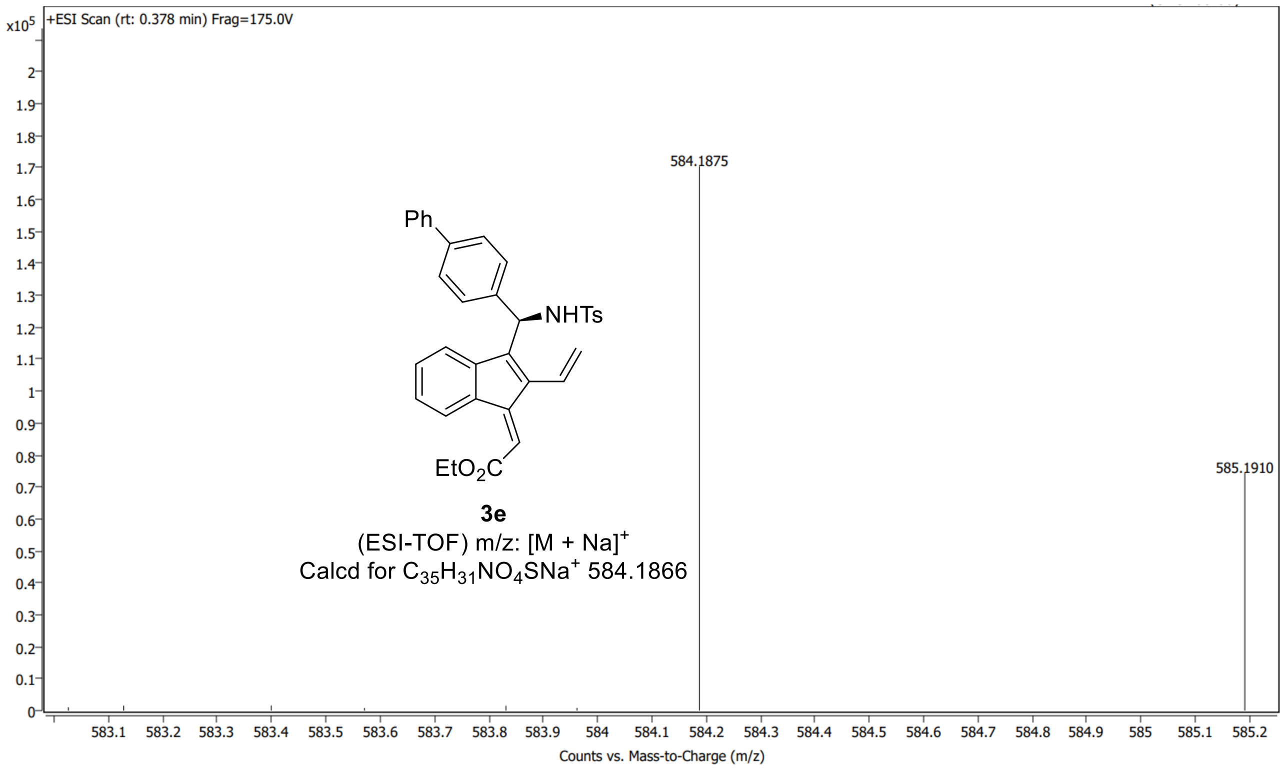
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.602 | BB | 0.31 | 630.9731 | 12771.9111 | 49.6368 |
| 10.893 | BB | 0.39 | 513.3306 | 12958.7939 | 50.3632 |
| | | | Totals: | 25730.7051 | 100.0000 |



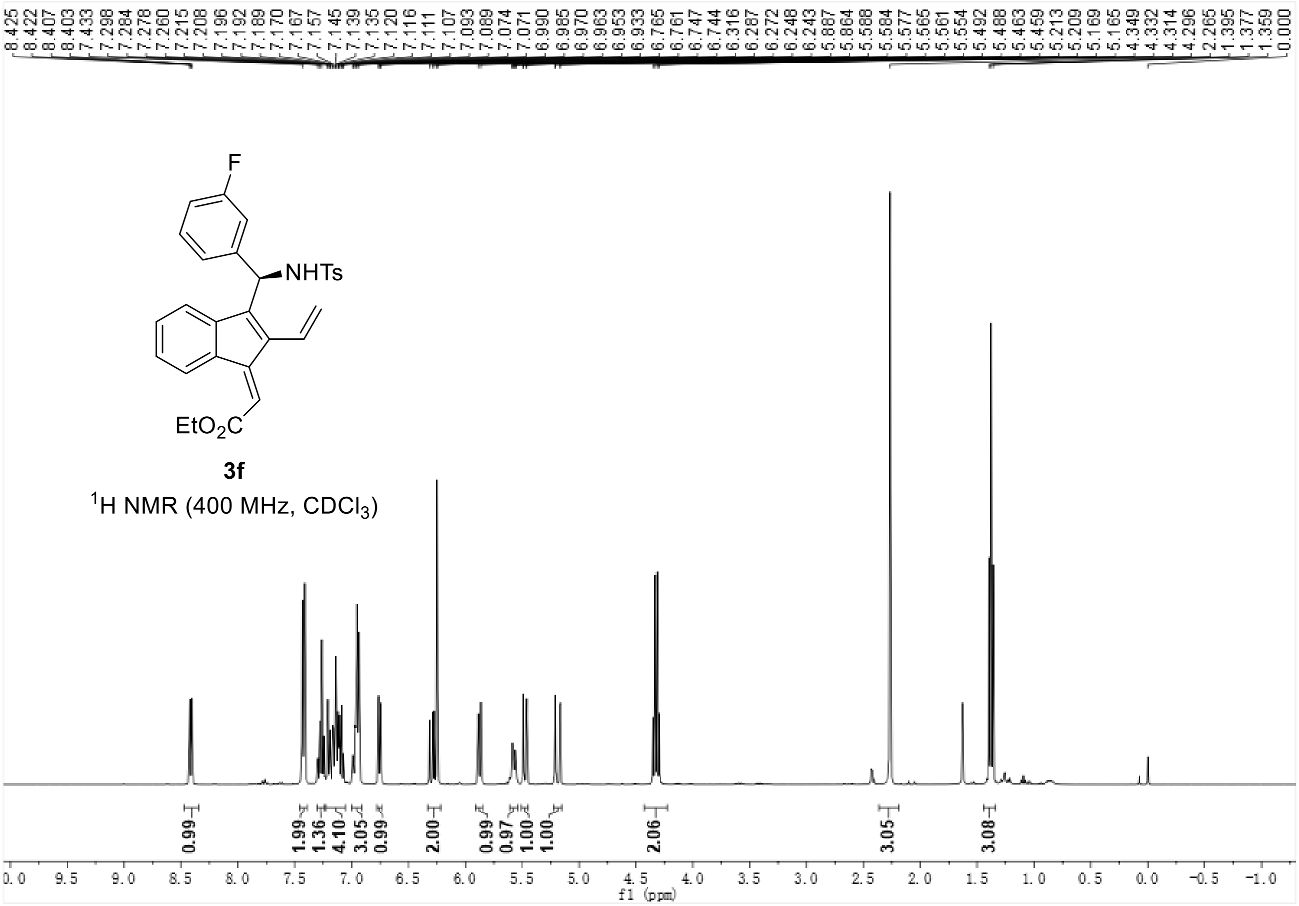
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.638 | BBA | 0.27 | 114.7376 | 1993.8225 | 4.0049 |
| 10.943 | BBA | 0.36 | 2053.2610 | 47791.1016 | 95.9951 |
| | | | Totals: | 49784.9241 | 100.0000 |



**3e**

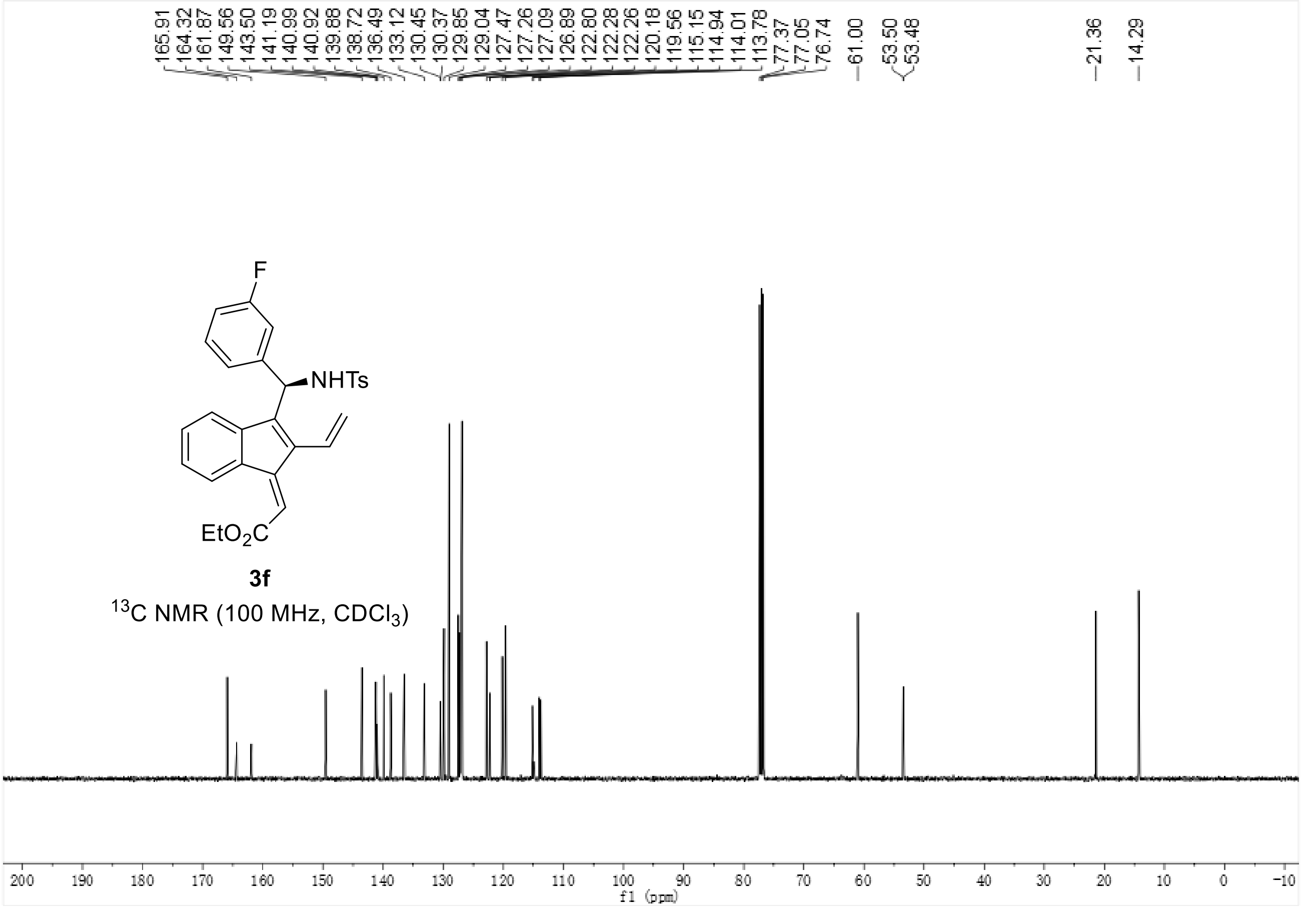
(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{35}H_{31}NO_4SNa^+$ 584.1866



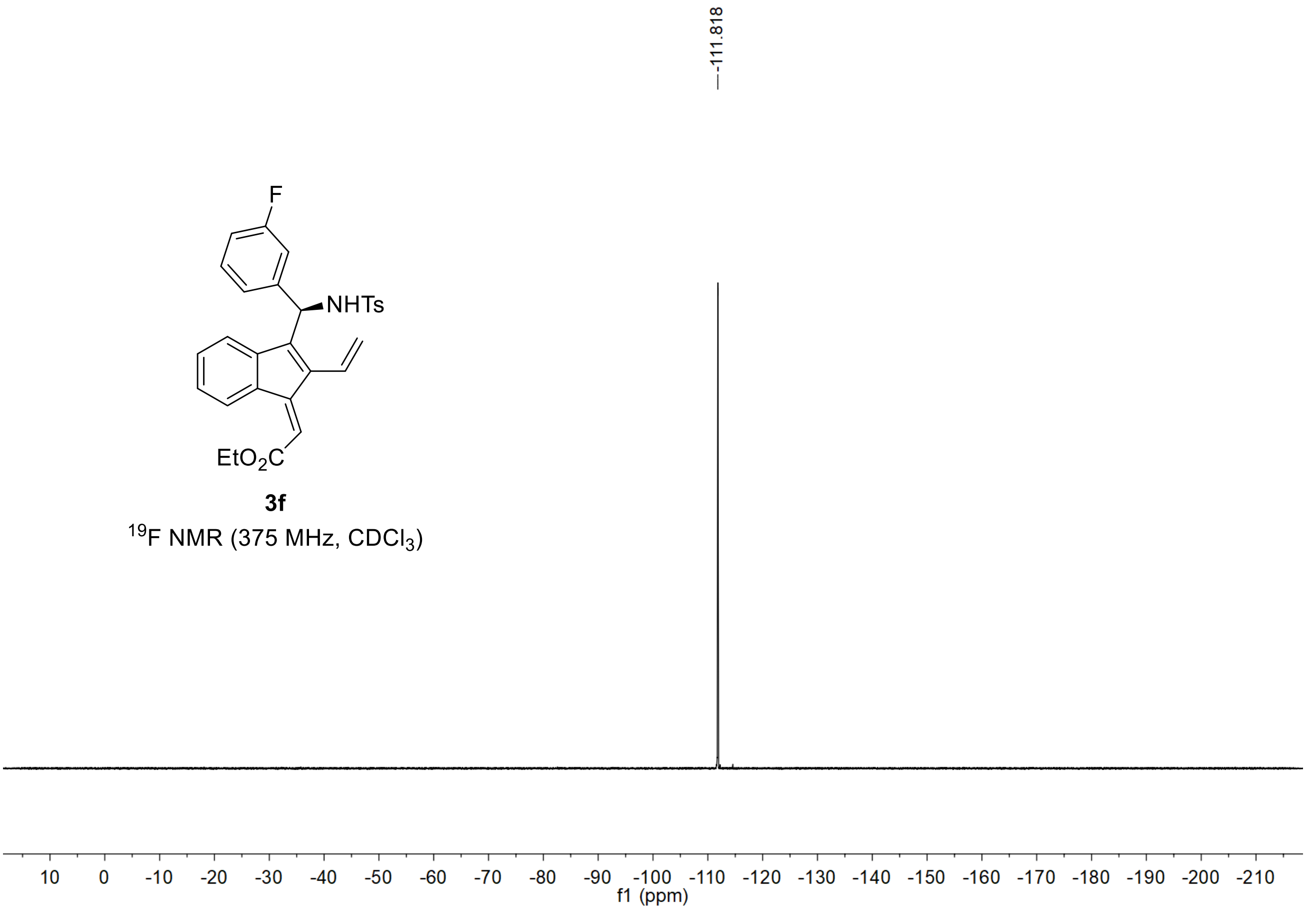
**3f**

$^1$H NMR (400 MHz, CDCl$_3$)



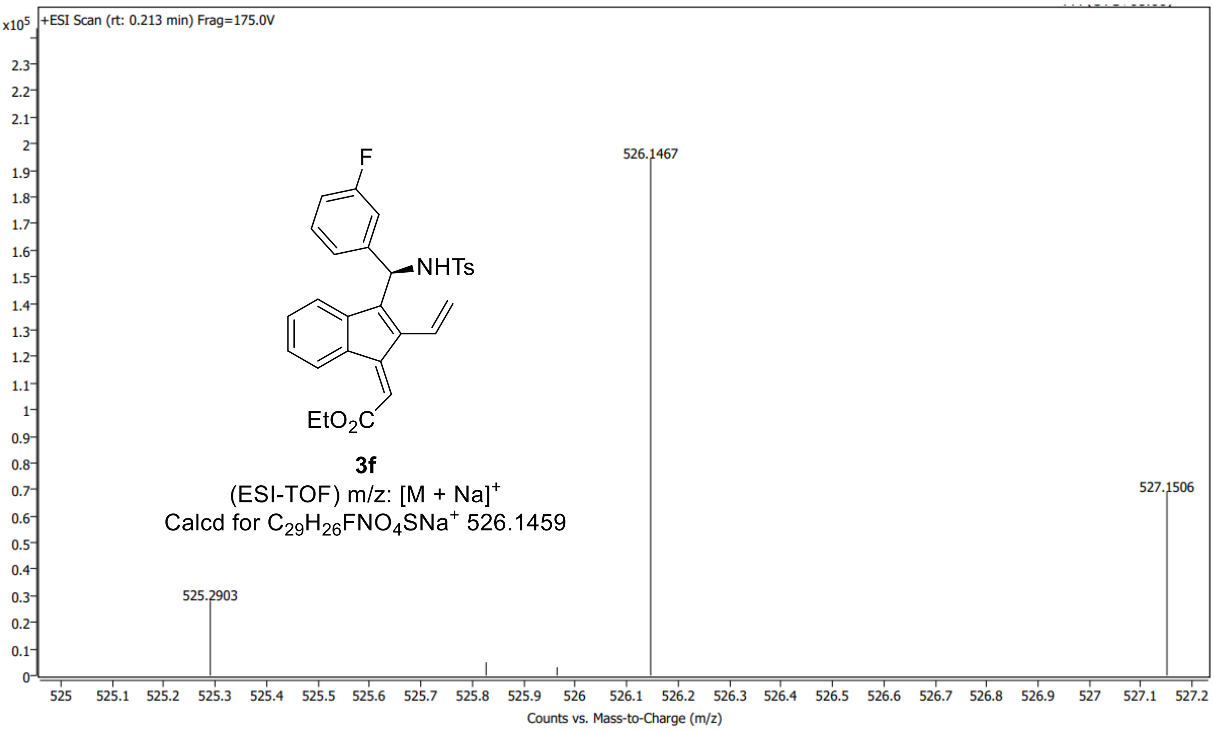
**3f**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**3f**

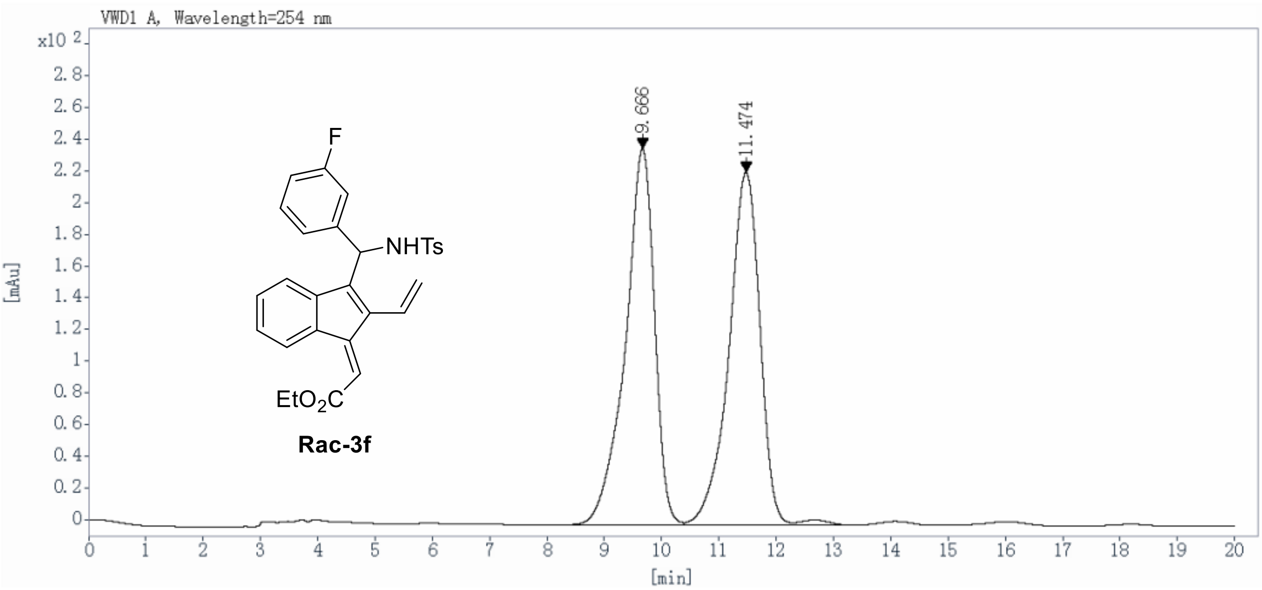
$^{19}$F NMR (375 MHz, CDCl$_3$)



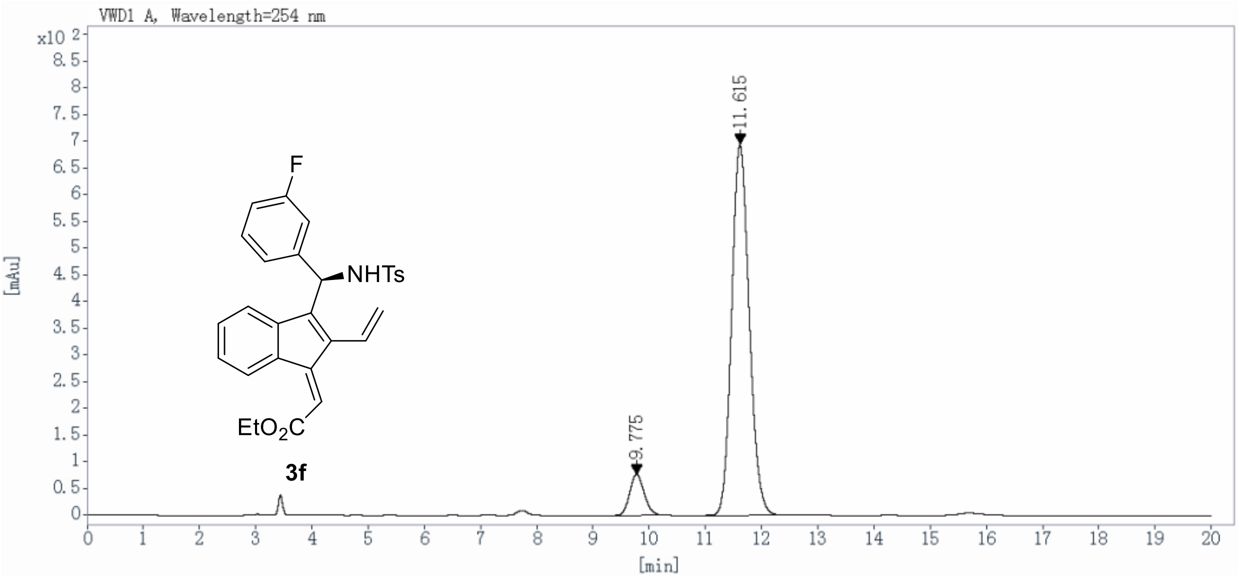
**3f**

(ESI-TOF) m/z: [M + Na]$^+$

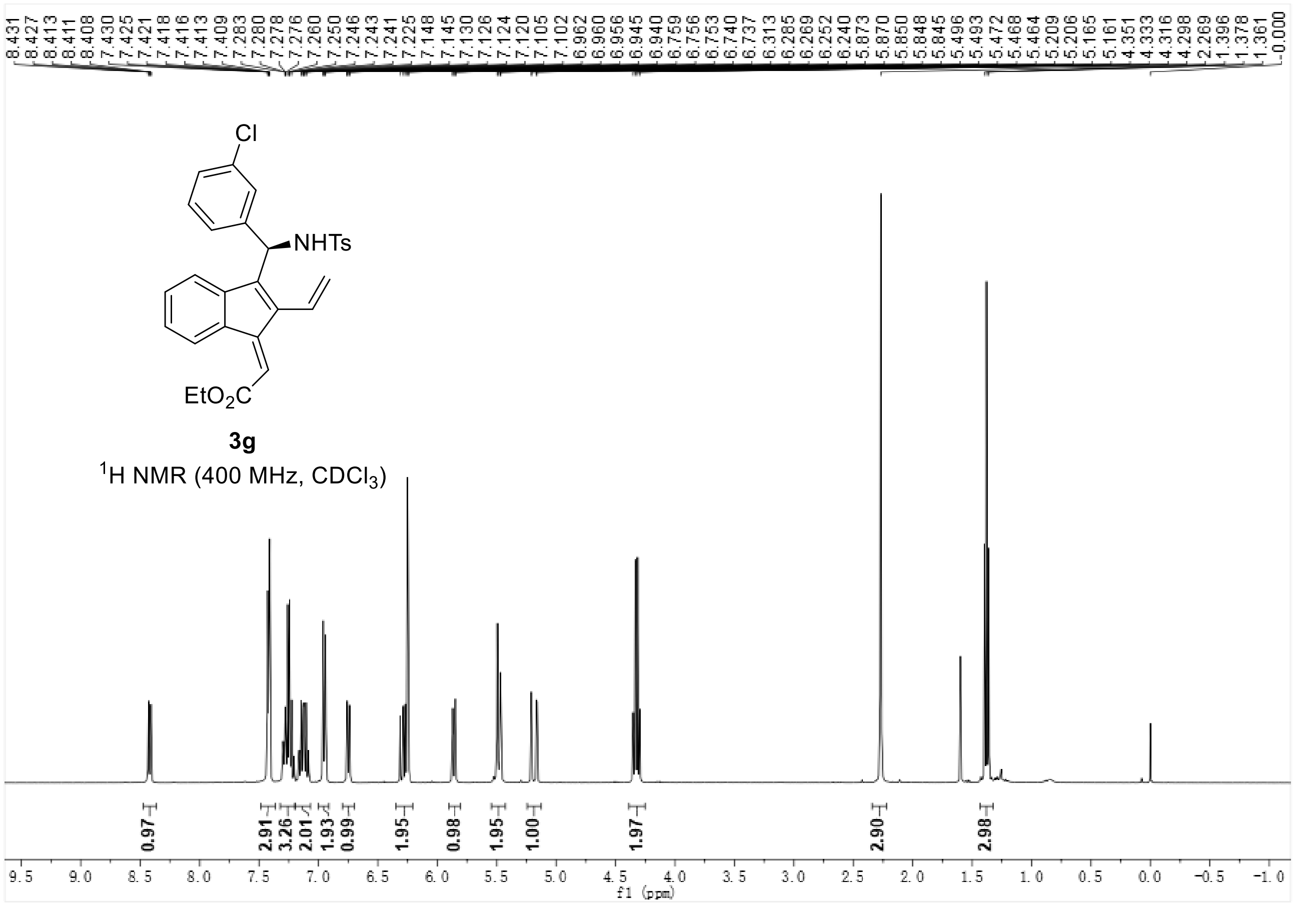
Calcd for $C_{29}H_{26}FNO_4SNa^+$ 526.1459



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.666 | BV | 0.53 | 237.1501 | 8408.0137 | 49.8295 |
| 11.474 | VV R | 0.58 | 222.3759 | 8465.5596 | 50.1705 |
| | | | Totals: | 16873.5732 | 100.0000 |

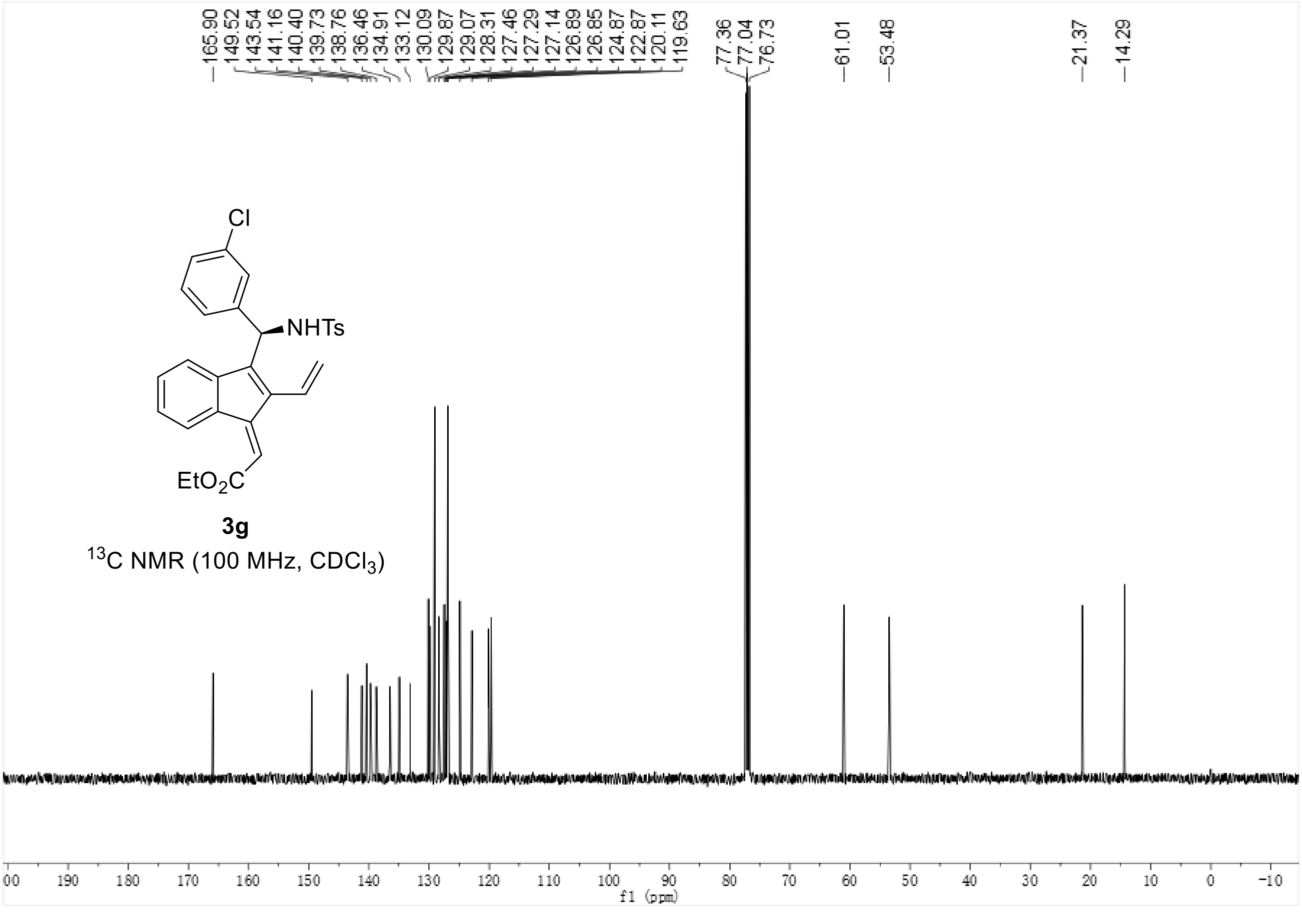


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.775 | BBA | 0.28 | 76.6214 | 1375.9526 | 8.3765 |
| 11.615 | BB | 0.34 | 694.0079 | 15050.3486 | 91.6235 |
| | | | Totals: | 16426.3013 | 100.0000 |



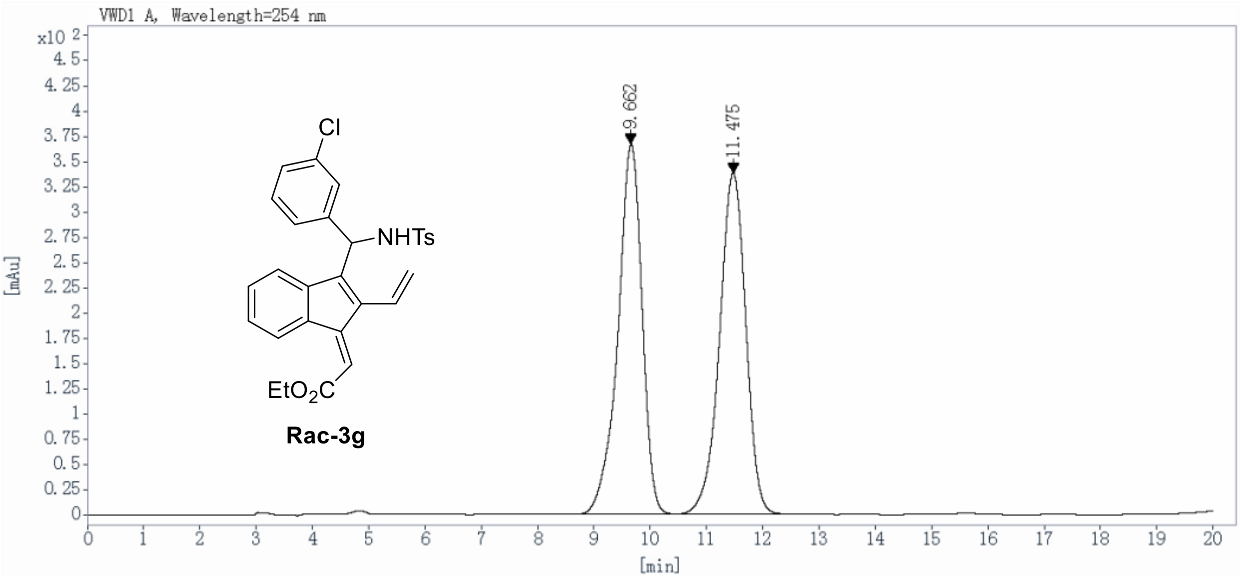
3g

$^1$H NMR (400 MHz, CDCl$_3$)

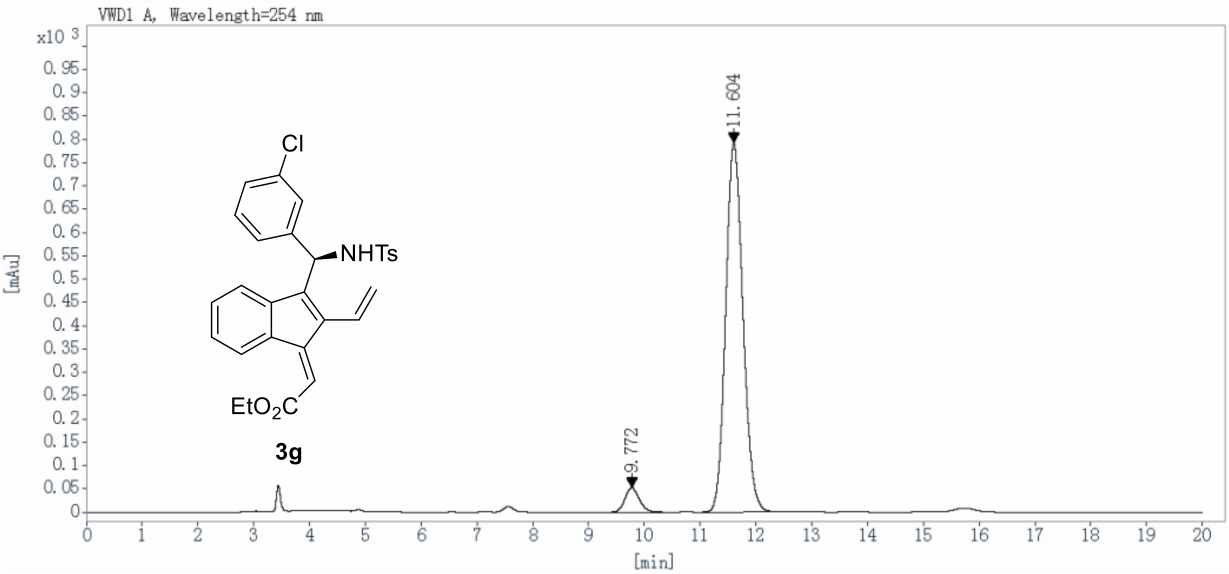


3g

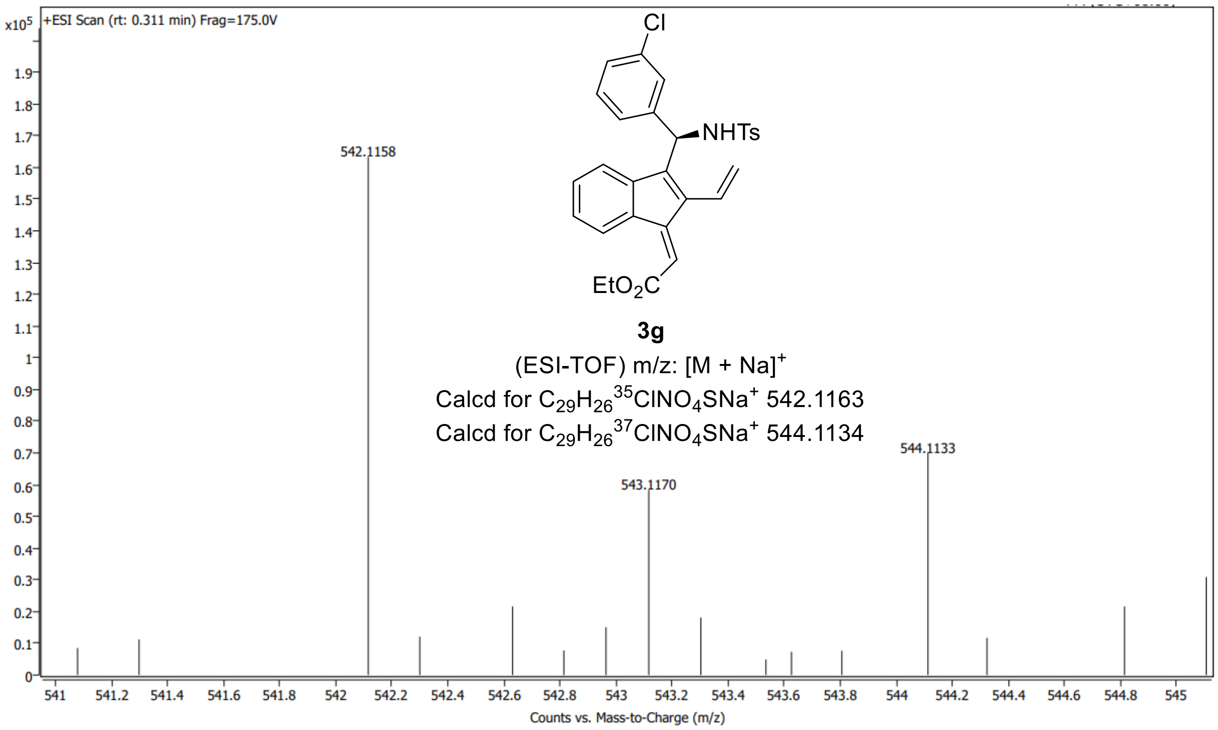
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.662 | BB | 0.46 | 366.3933 | 10941.8984 | 50.0252 |
| 11.475 | BB | 0.50 | 337.7645 | 10930.8682 | 49.9748 |
|  |  |  | Totals: | 21872.7666 | 100.0000 |



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.772 | BBA | 0.27 | 52.1811 | 922.5963 | 5.1395 |
| 11.604 | BB | 0.33 | 791.5866 | 17028.6543 | 94.8605 |
|  |  |  | Totals: | 17951.2506 | 100.0000 |

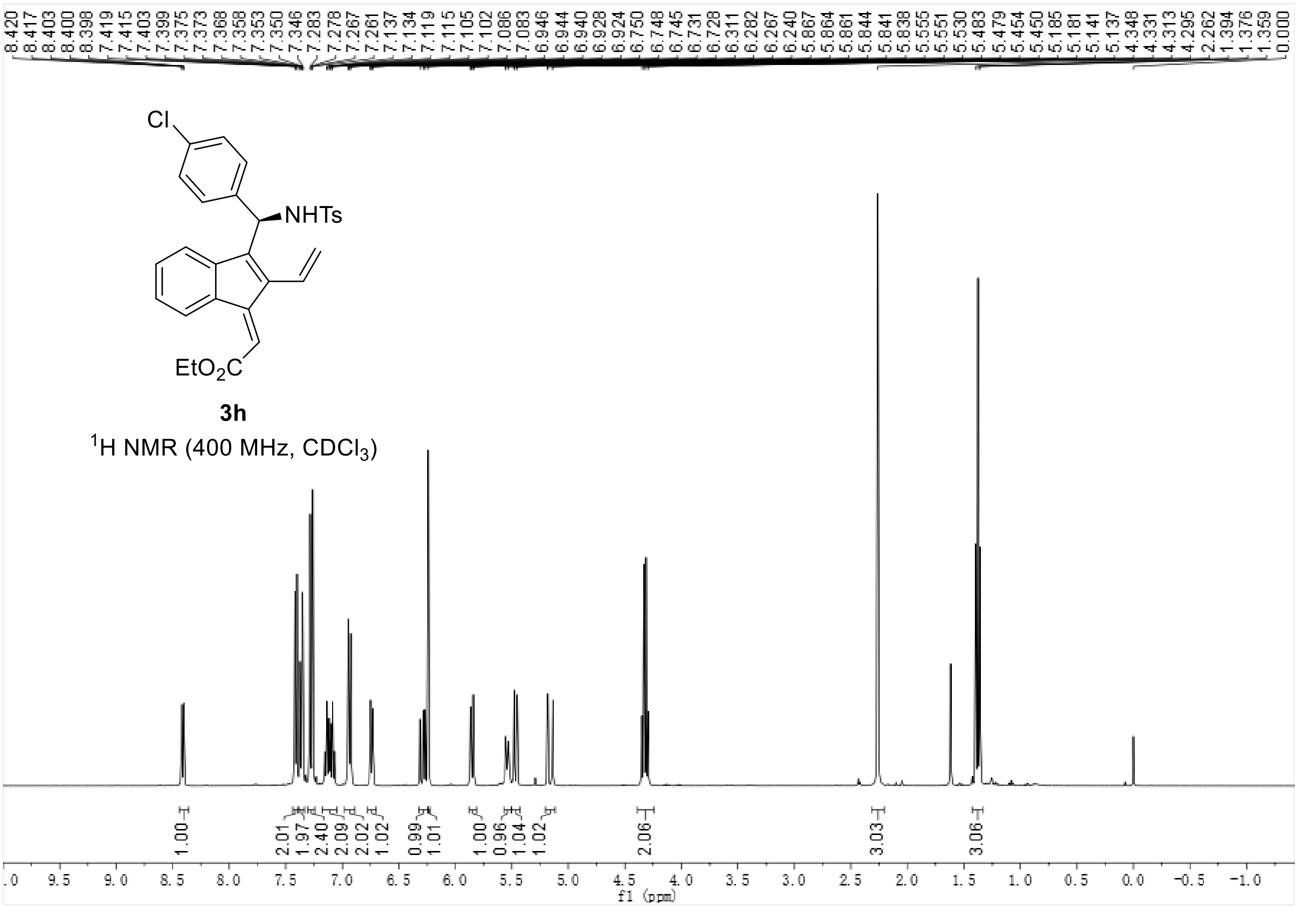


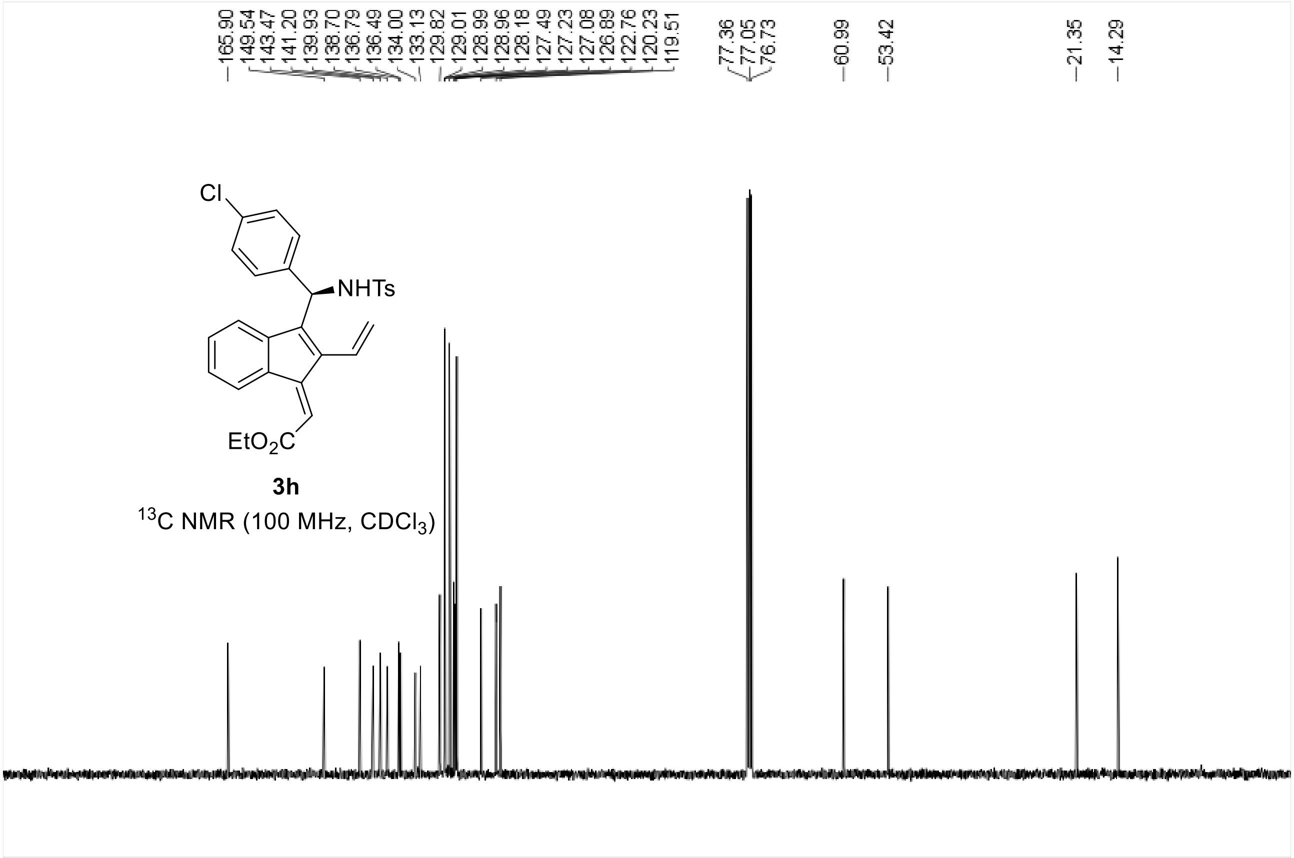
**3g**

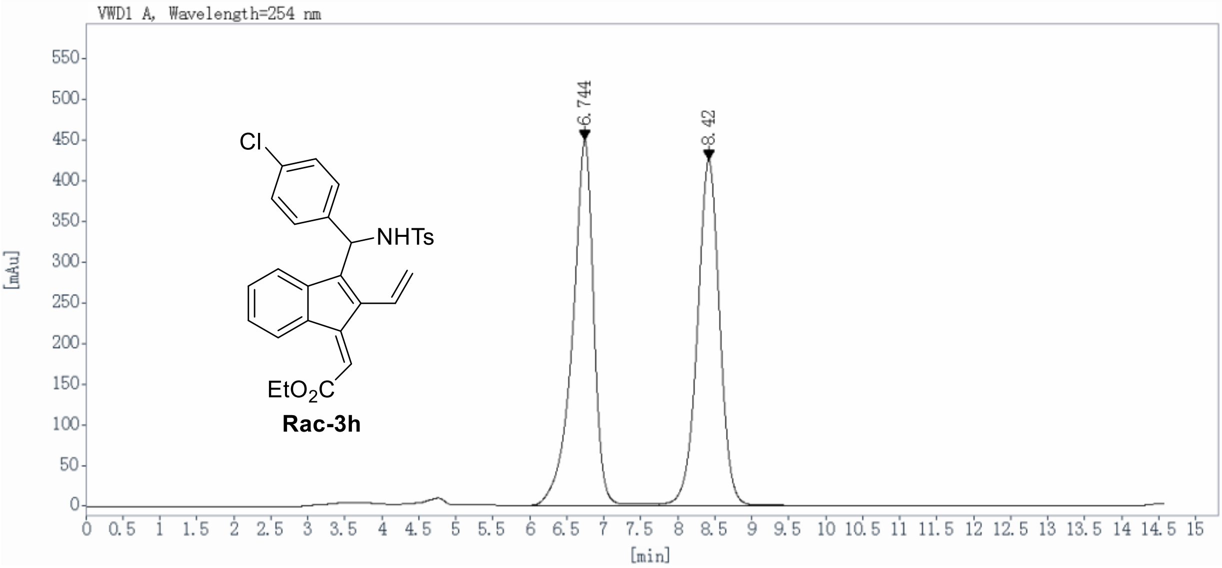
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163

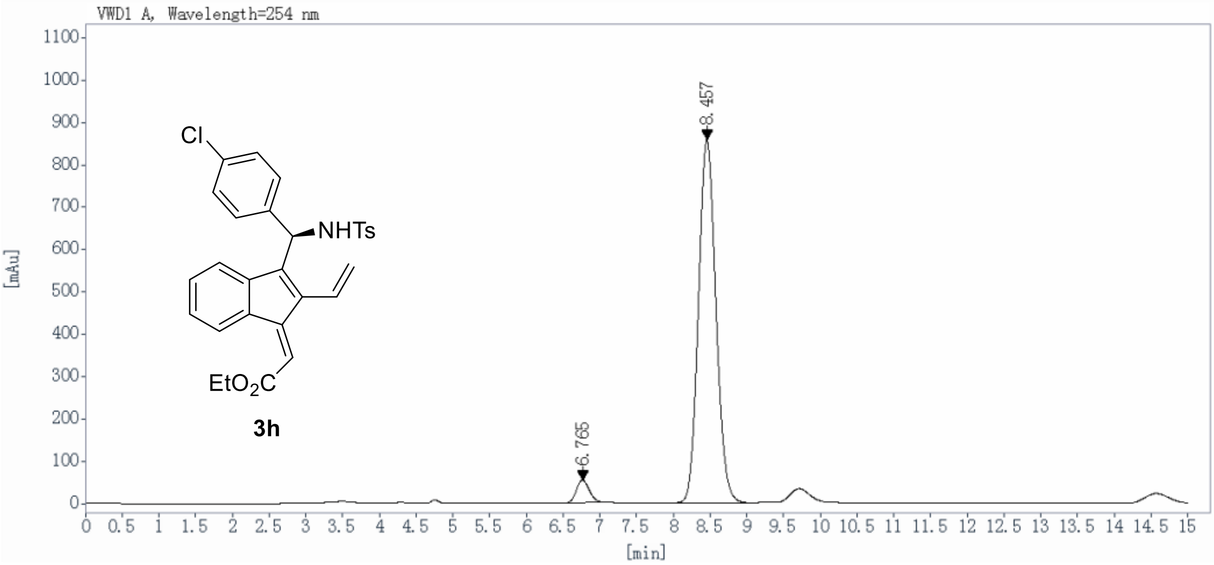
Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134


8.420
8.417
8.403
8.400
8.398
7.419
7.415
7.403
7.399
7.375
7.373
7.368
7.358
7.353
7.350
7.346
7.283
7.278
7.267
7.261
7.137
7.134
7.119
7.115
7.105
7.102
7.086
7.083
6.946
6.944
6.940
6.928
6.924
6.750
6.748
6.745
6.731
6.728
6.311
6.282
6.267
6.240
5.867
5.864
5.861
5.844
5.841
5.838
5.555
5.551
5.530
5.483
5.479
5.454
5.450
5.185
5.181
5.141
5.137
4.348
4.331
4.313
4.295
2.262
1.394
1.376
1.359
0.000
Cl
NHTs
EtO2C
3h
1H NMR (400 MHz, CDCl3)
1.00
2.01
1.97
2.40
2.09
2.02
1.02
0.99
1.01
1.00
0.96
1.04
1.02
2.06
3.03
3.06
f1 (ppm)

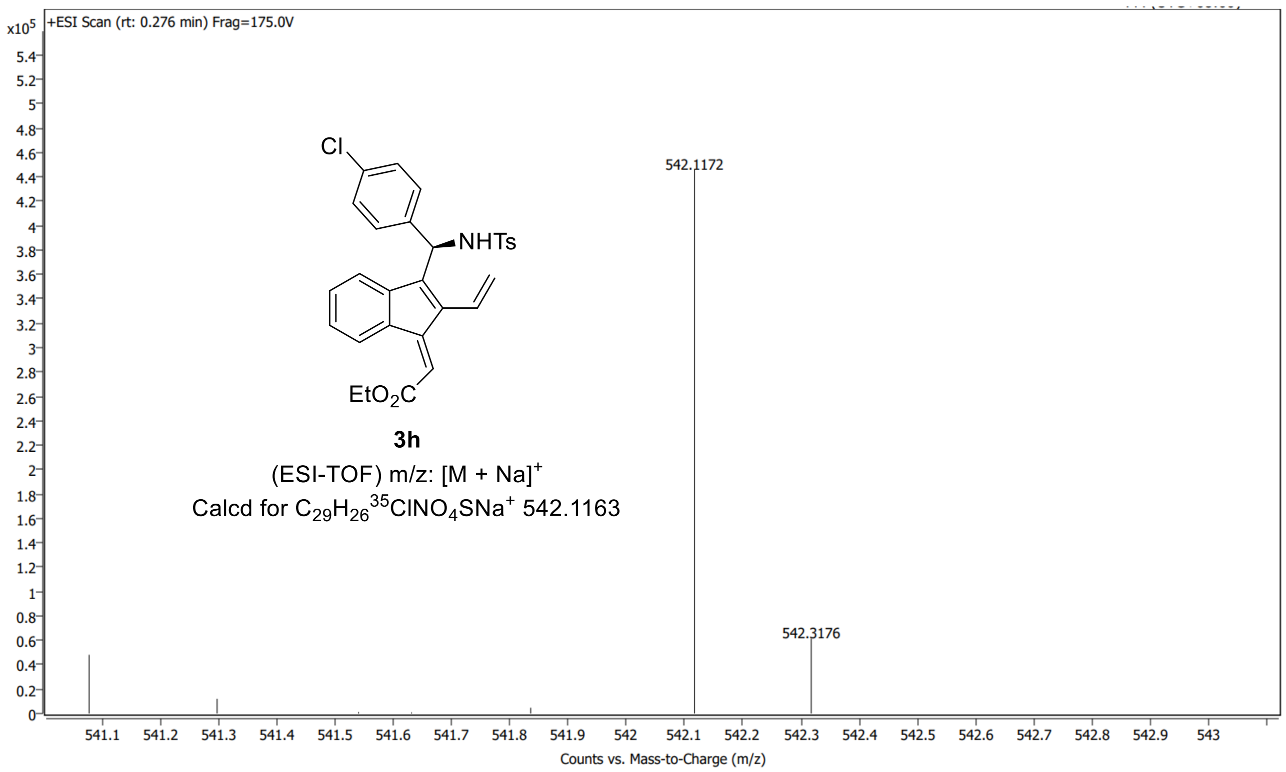

165.90
149.54
143.47
141.20
139.93
138.70
136.79
136.49
134.00
133.13
129.82
129.01
128.96
128.18
127.49
127.23
127.08
126.89
122.76
120.23
119.51
77.36
77.05
76.73
60.99
53.42
21.35
14.29
Cl
NHTs
EtO2C
3h
13C NMR (100 MHz, CDCl3)
f1 (ppm)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.744 | BV R | 0.29 | 449.0412 | 8966.7578 | 50.1695 |
| 8.420 | VV R | 0.32 | 424.7675 | 8906.1768 | 49.8305 |
|  |  |  | Totals: | 17872.9346 | 100.0000 |



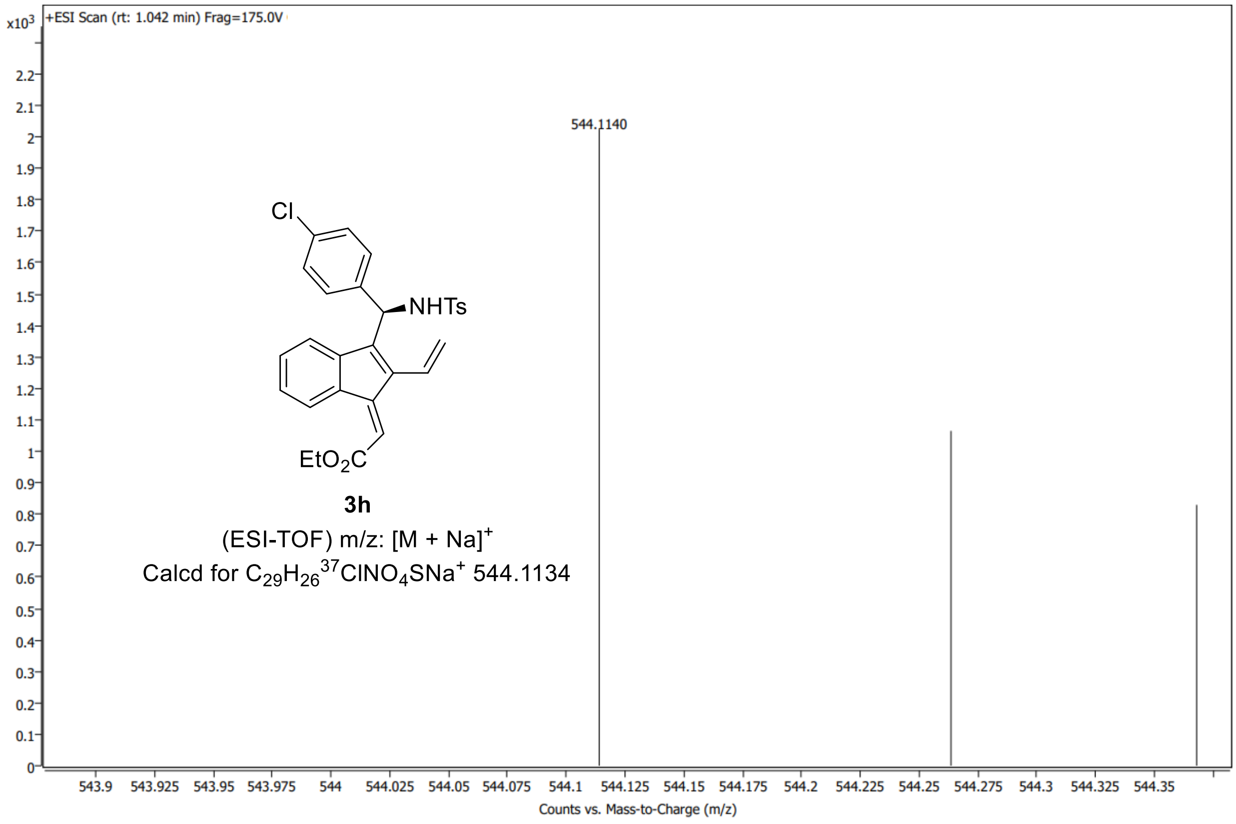
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.765 | BBA | 0.19 | 52.9751 | 634.1752 | 4.2940 |
| 8.457 | BB | 0.26 | 857.6638 | 14134.7295 | 95.7060 |
|  |  |  | Totals: | 14768.9047 | 100.0000 |



**3h**

(ESI-TOF) m/z: $[M + Na]^+$

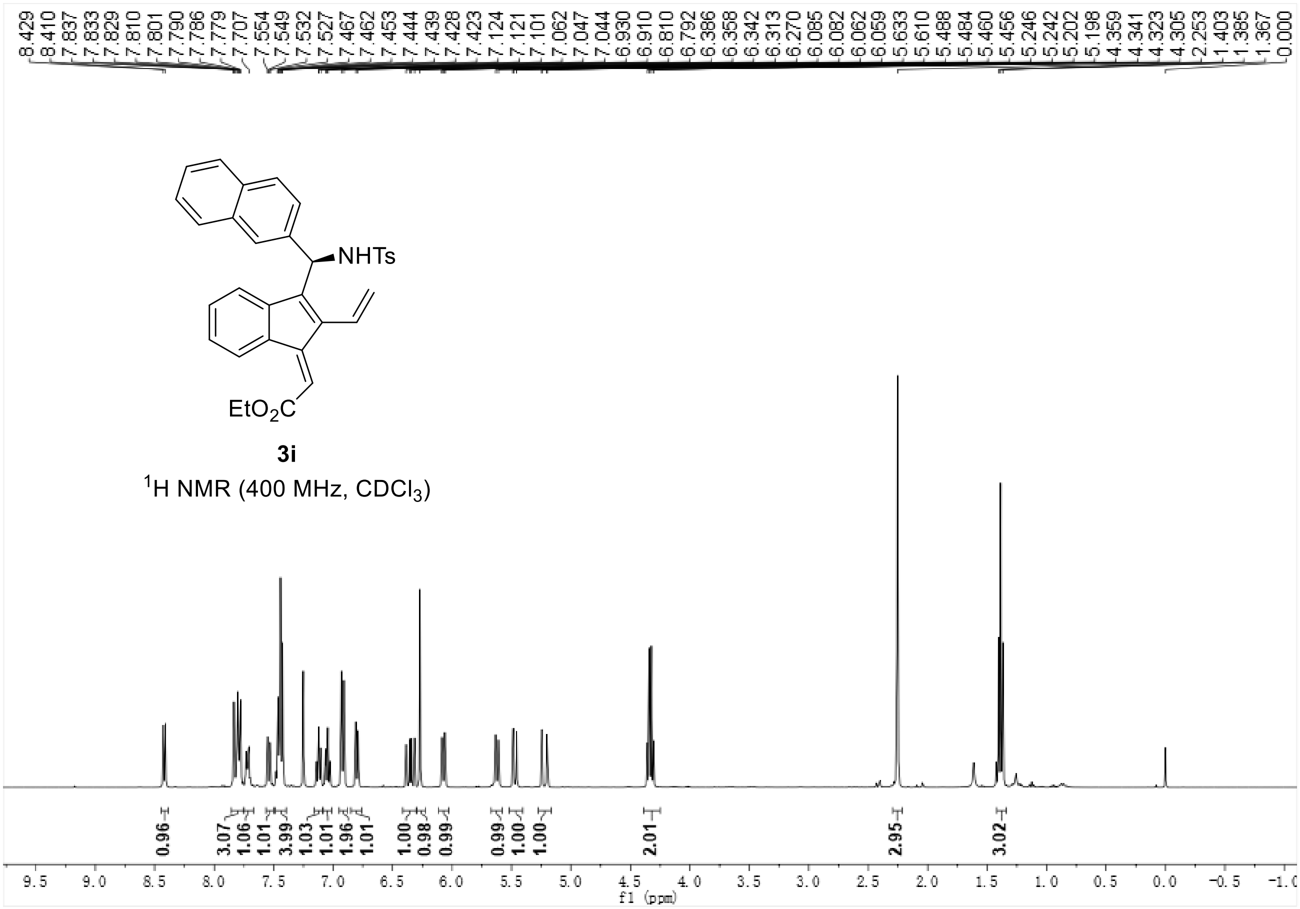
Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163

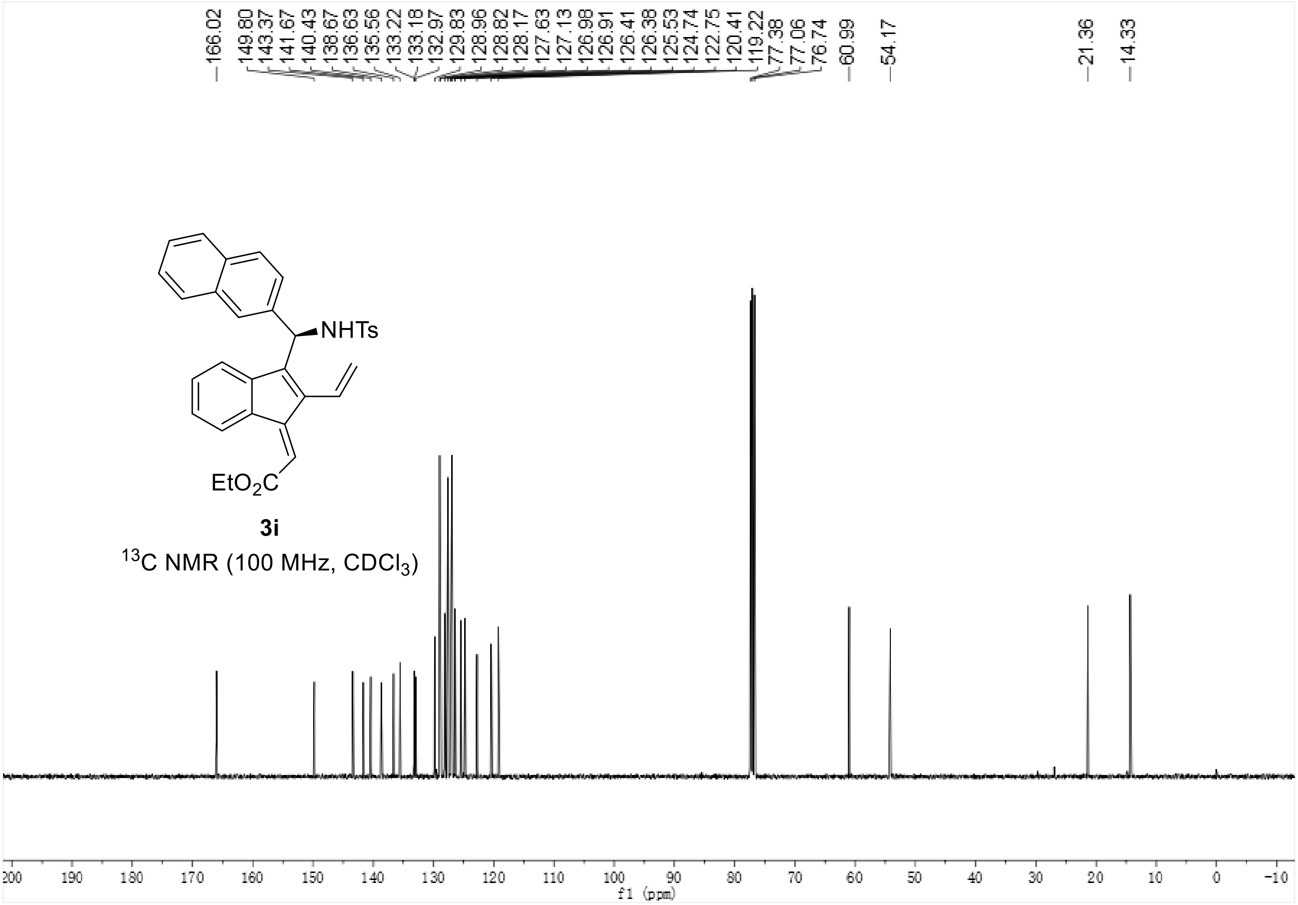


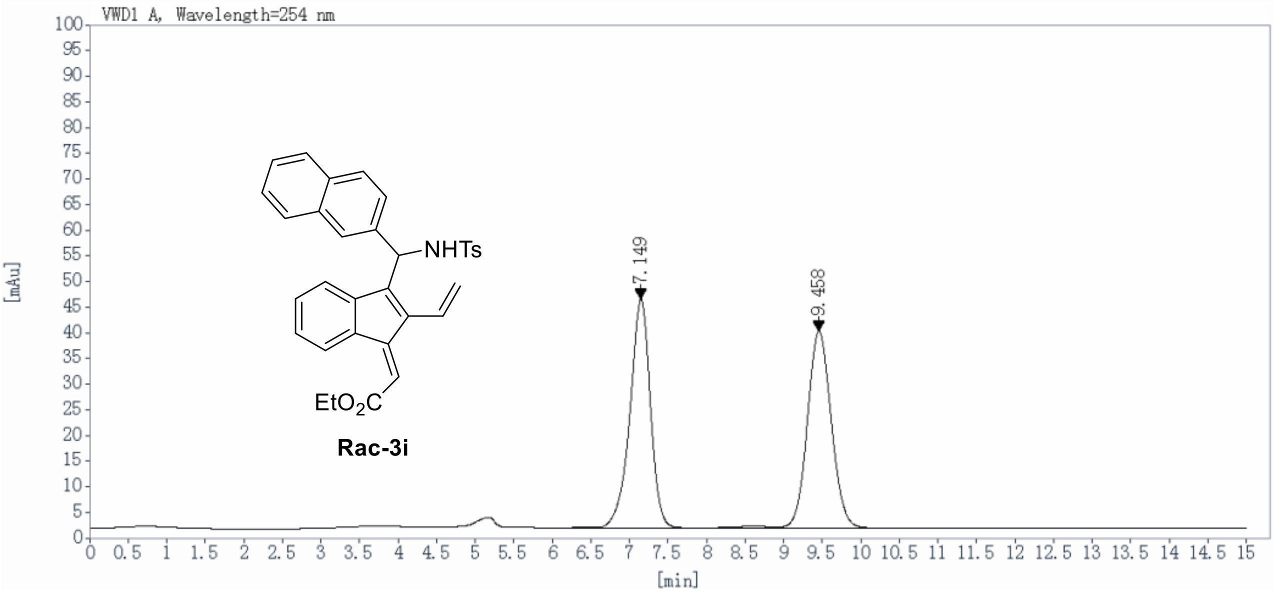
**3h**

(ESI-TOF) m/z: $[M + Na]^+$

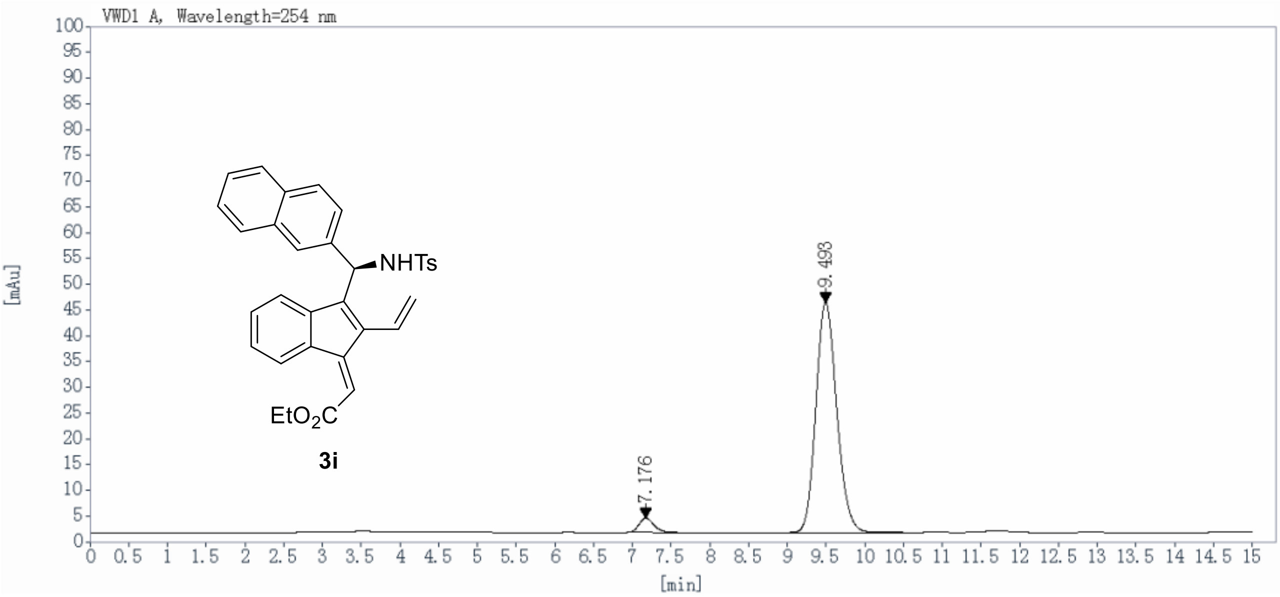
Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134


8.429
8.410
7.837
7.833
7.829
7.810
7.801
7.790
7.786
7.779
7.707
7.554
7.549
7.532
7.527
7.467
7.462
7.453
7.444
7.439
7.428
7.423
7.124
7.121
7.101
7.062
7.047
7.044
6.930
6.910
6.810
6.792
6.386
6.358
6.342
6.313
6.270
6.085
6.082
6.062
6.059
5.633
5.610
5.488
5.484
5.460
5.456
5.246
5.242
5.202
5.198
4.359
4.341
4.323
4.305
2.253
1.403
1.385
1.367
0.000
NHTs
EtO$_2$C
3i
$^1$H NMR (400 MHz, CDCl$_3$)
0.96
3.07
1.06
1.01
3.99
1.03
1.01
1.96
1.01
1.00
0.98
0.99
0.99
1.00
1.00
2.01
2.95
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

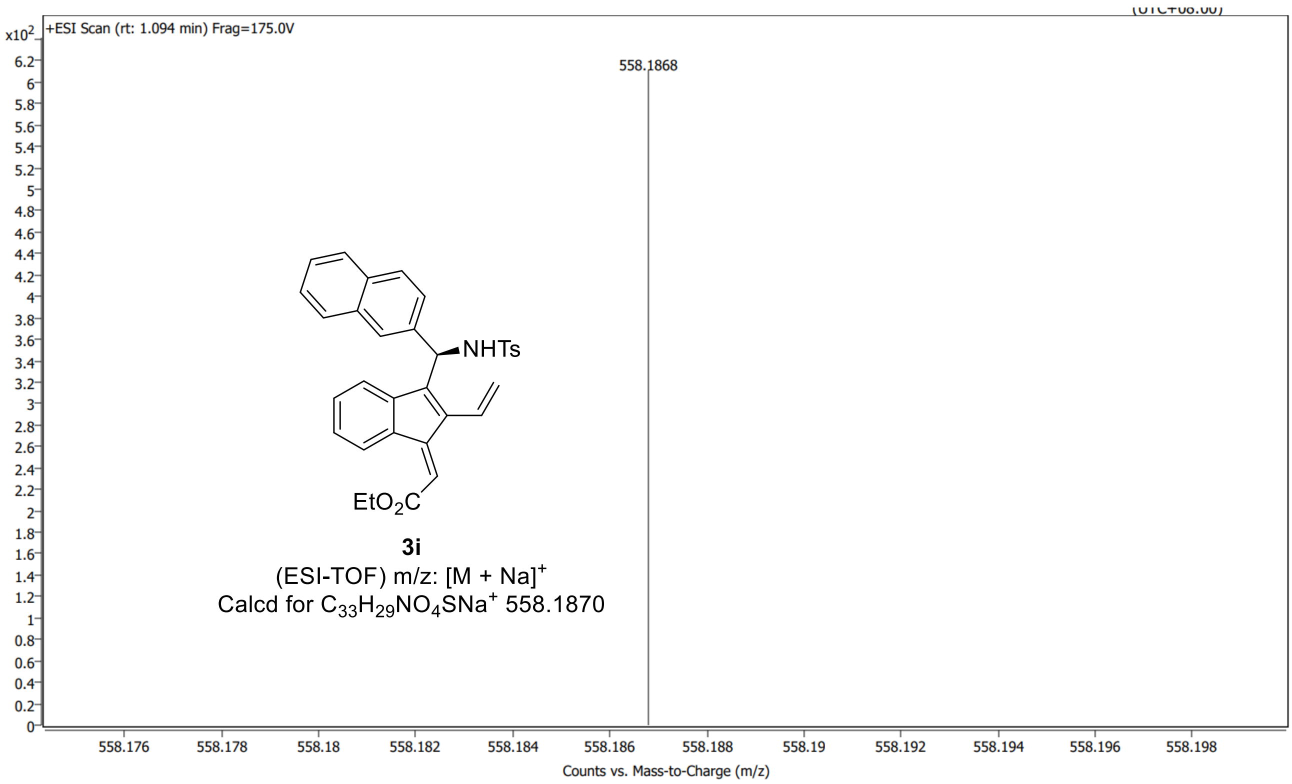

166.02
149.80
143.37
141.67
140.43
138.67
136.63
135.56
133.22
133.18
132.97
129.83
128.96
128.82
128.17
127.63
127.13
126.98
126.91
126.41
126.38
125.53
124.74
122.75
120.41
119.22
77.38
77.06
76.74
60.99
54.17
21.36
14.33
NHTs
EtO$_2$C
3i
$^{13}$C NMR (100 MHz, CDCl$_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.149 | VB R | 0.28 | 412.5558 | 7639.4331 | 49.6618 |
| 9.458 | VB R | 0.33 | 355.0036 | 7743.4707 | 50.3382 |
| | | | Totals: | 15382.9038 | 100.0000 |



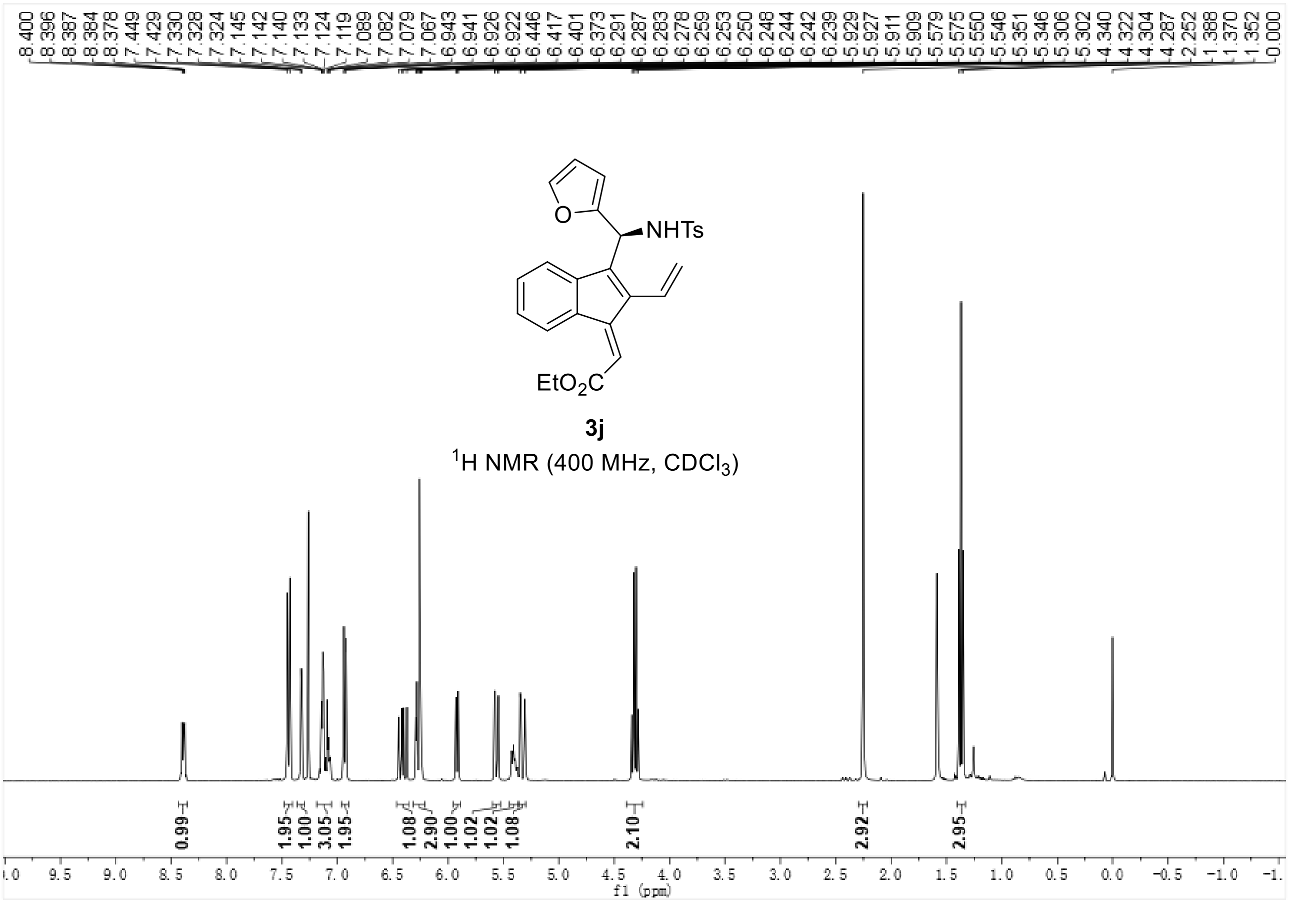
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.176 | BBA | 0.21 | 74.9665 | 991.3522 | 4.1266 |
| 9.493 | BB | 0.29 | 1228.7633 | 23032.3984 | 95.8734 |
| | | | Totals: | 24023.7507 | 100.0000 |



**3i**

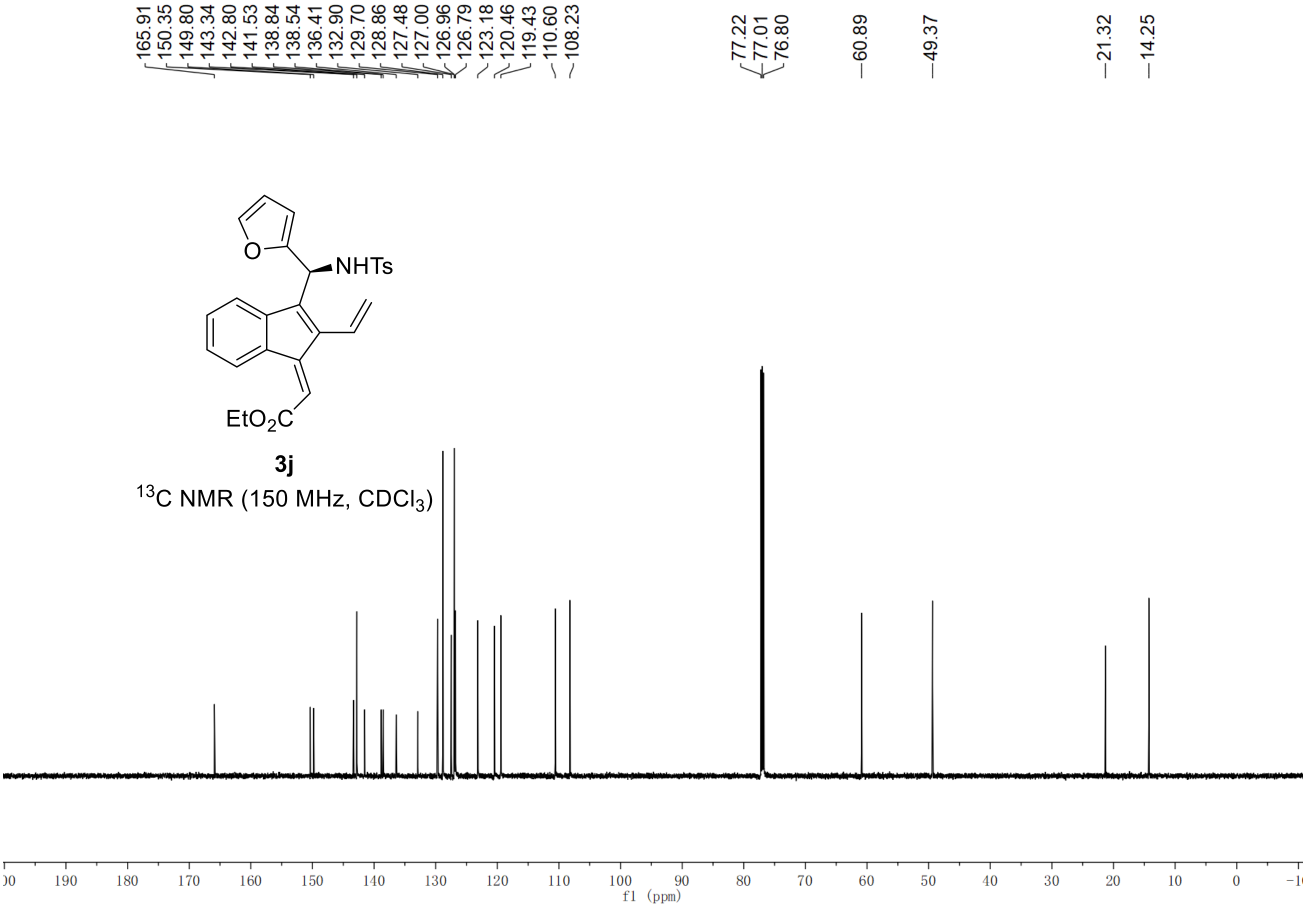
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{29}NO_4SNa^+$ 558.1870



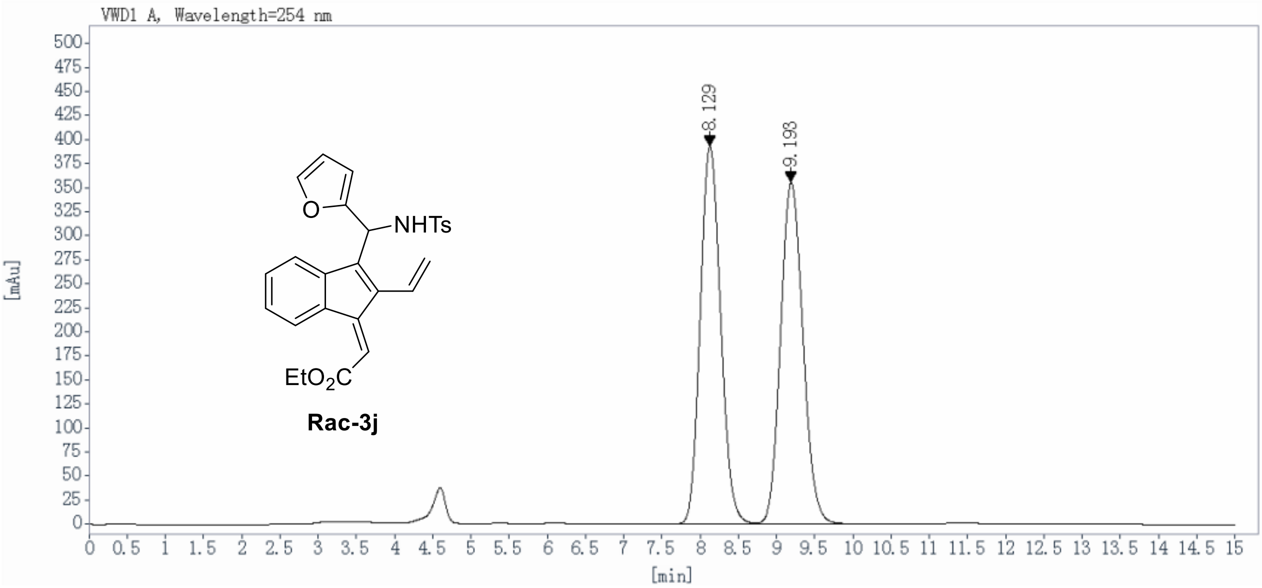
**3j**

$^1$H NMR (400 MHz, CDCl$_3$)



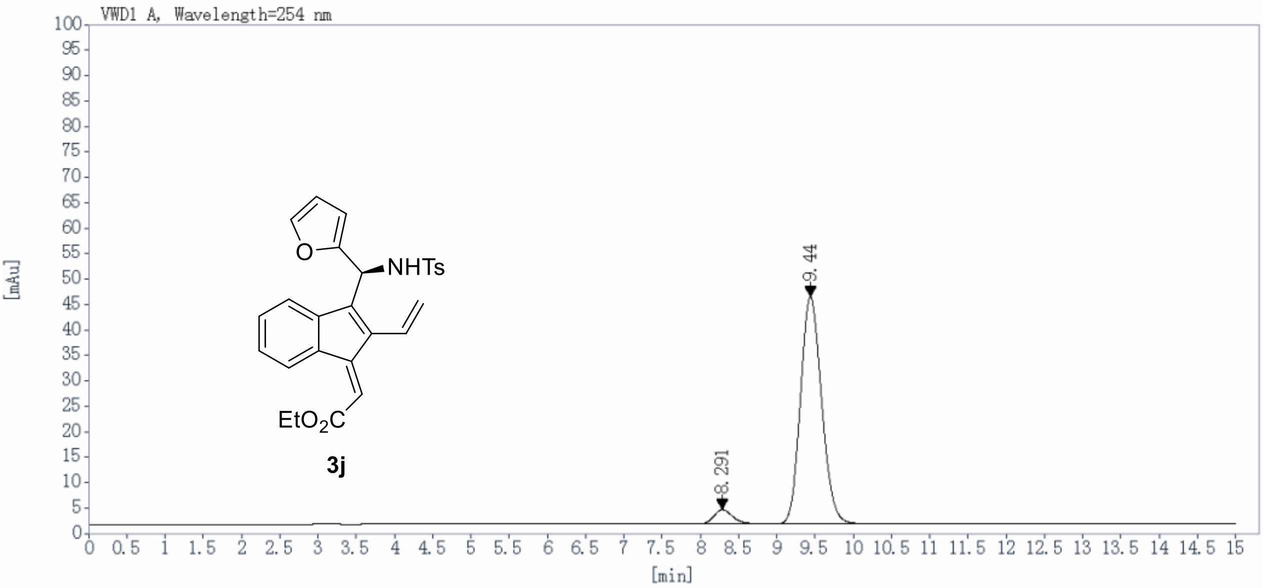
**3j**

$^{13}$C NMR (150 MHz, CDCl$_3$)



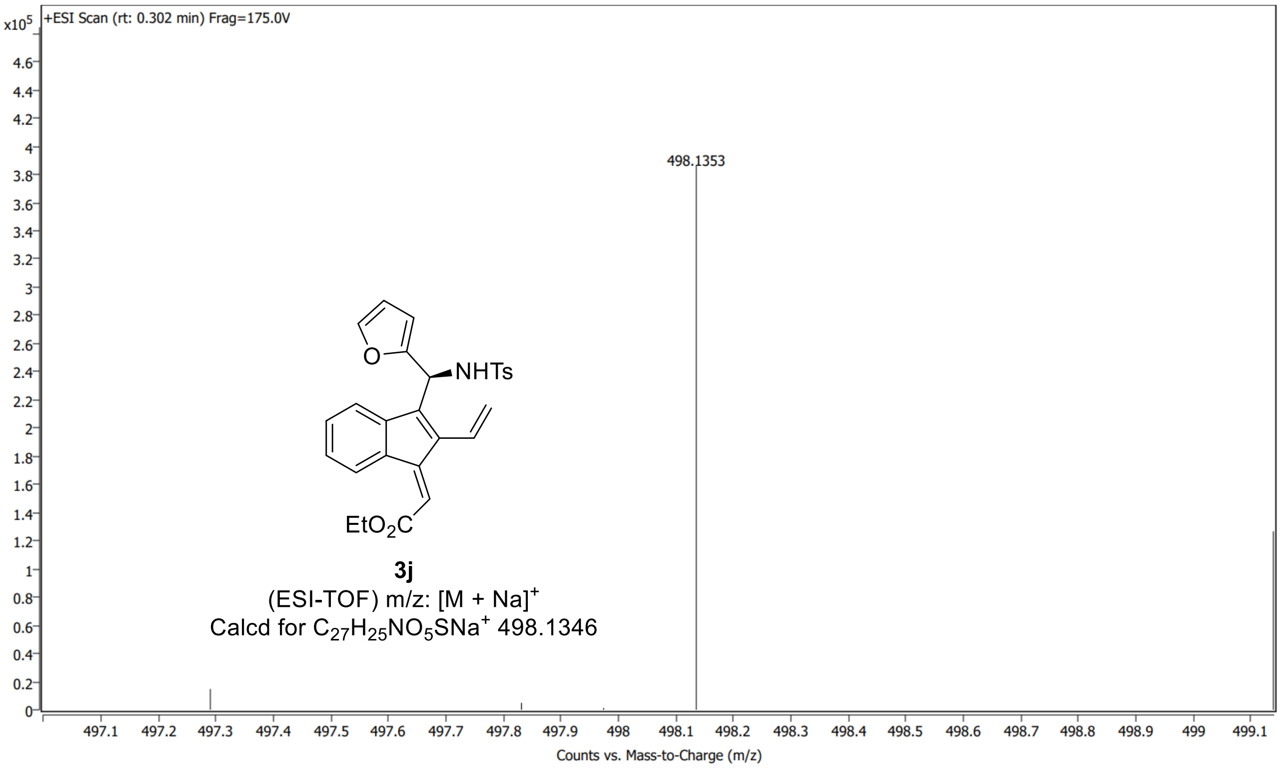
**Rac-3j**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.129 | VV R | 0.29 | 392.9979 | 7281.9351 | 50.1327 |
| 9.193 | VB | 0.32 | 355.3060 | 7243.3955 | 49.8673 |
| | | | Totals: | 14525.3306 | 100.0000 |



**3j**

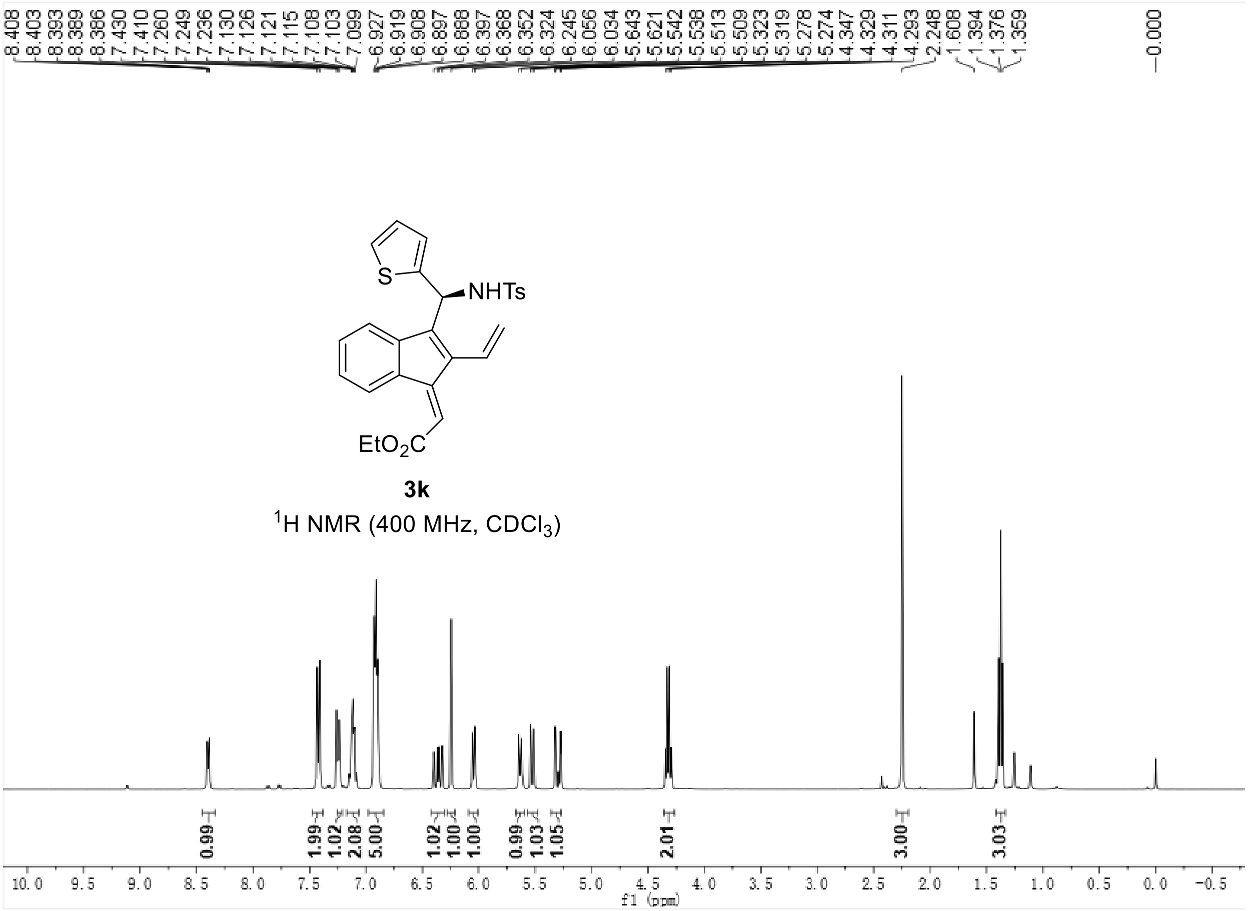
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.291 | BBA | 0.26 | 49.4906 | 822.5424 | 5.0977 |
| 9.440 | BB | 0.30 | 796.1212 | 15313.0176 | 94.9023 |
| | | | Totals: | 16135.5599 | 100.0000 |



**3j**

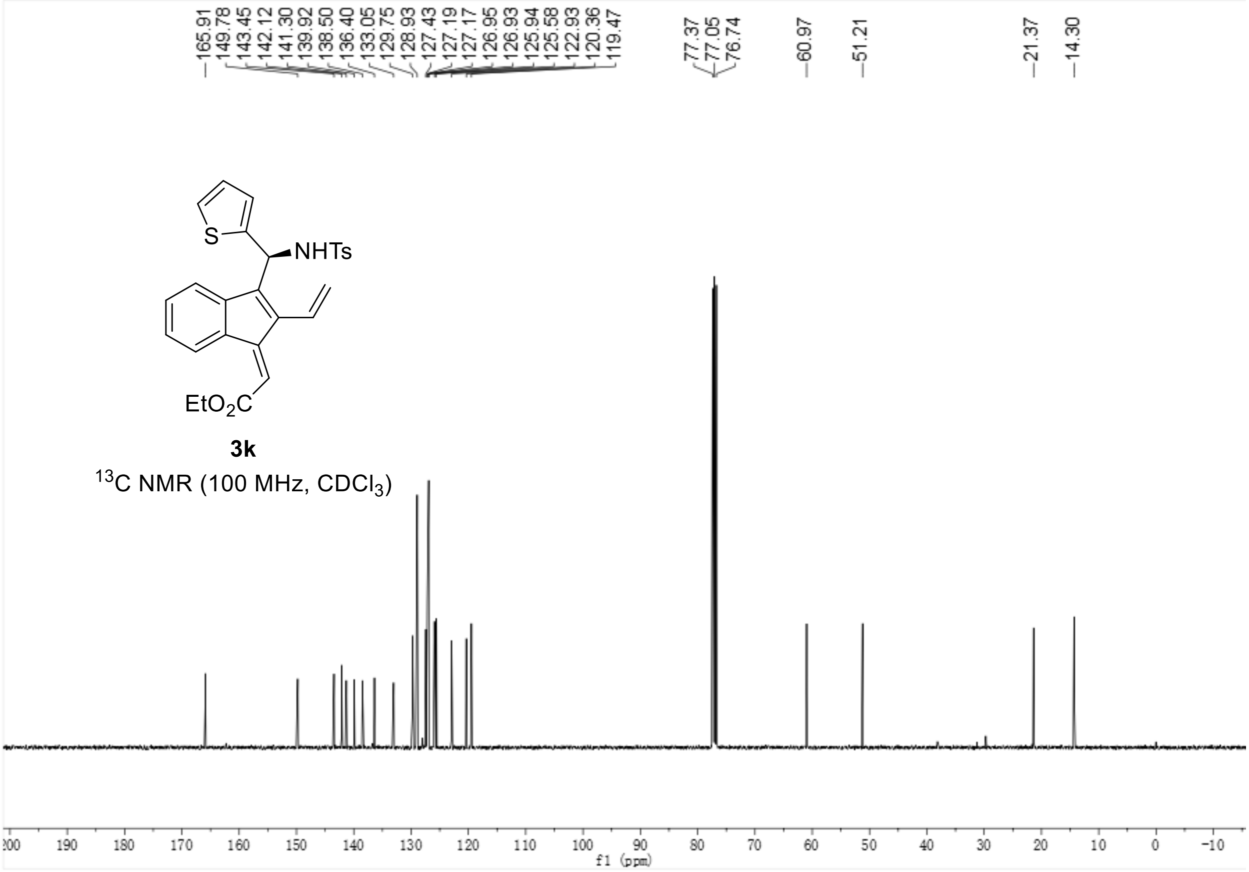
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{27}H_{25}NO_5SNa^+$ 498.1346



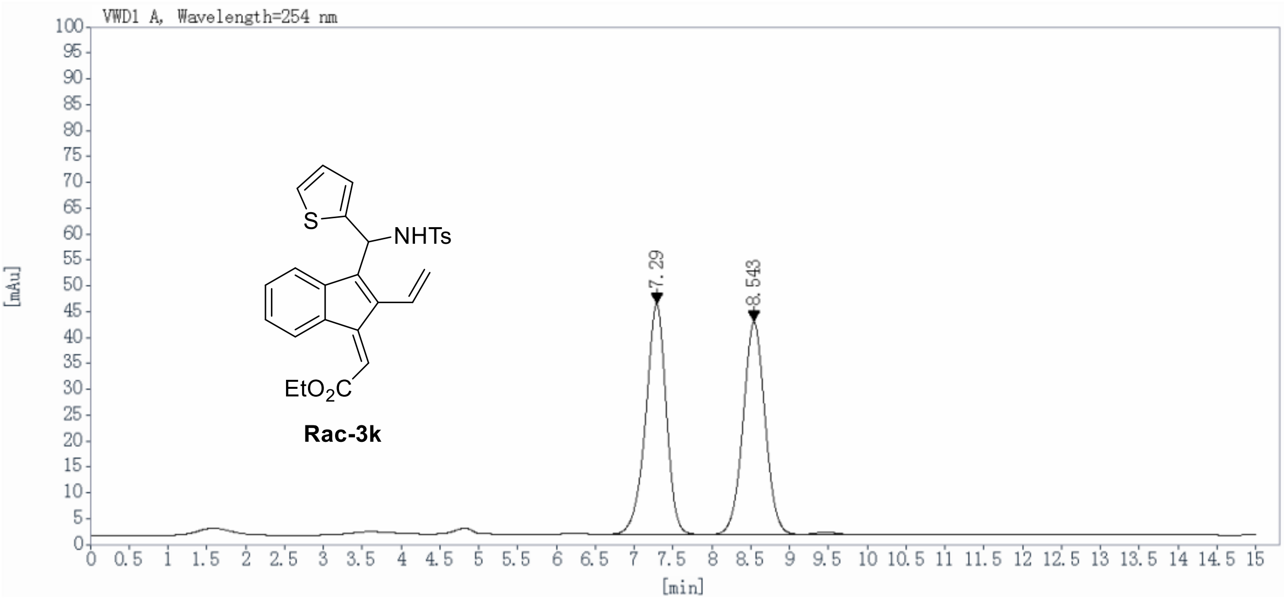
**3k**

$^1$H NMR (400 MHz, CDCl$_3$)

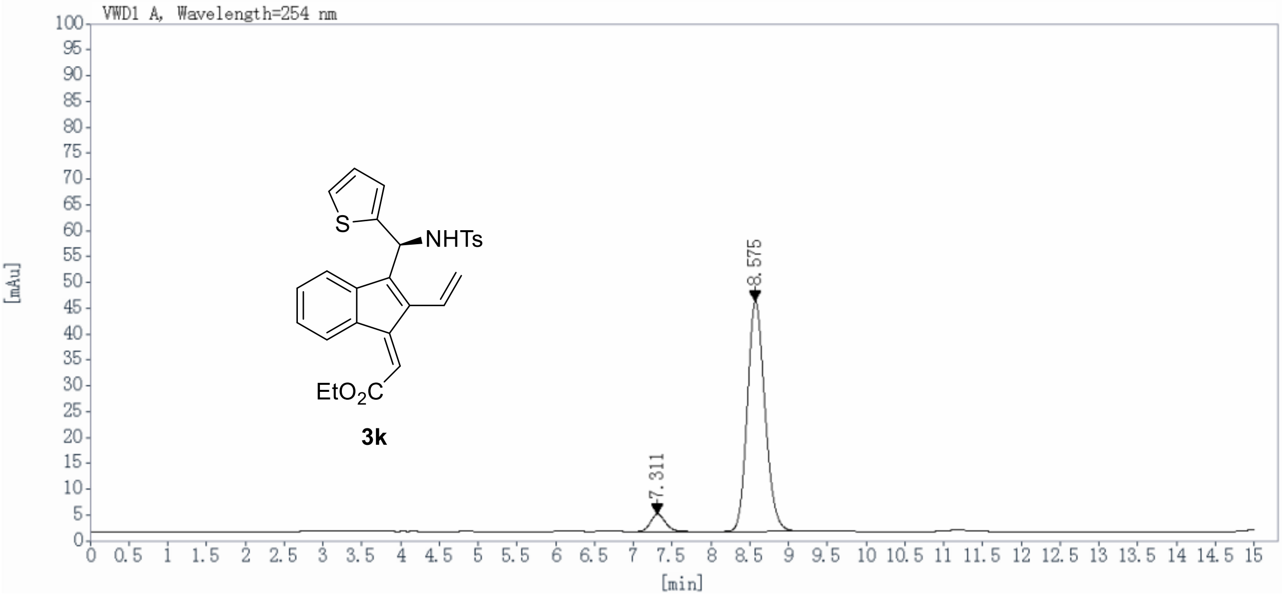


**3k**

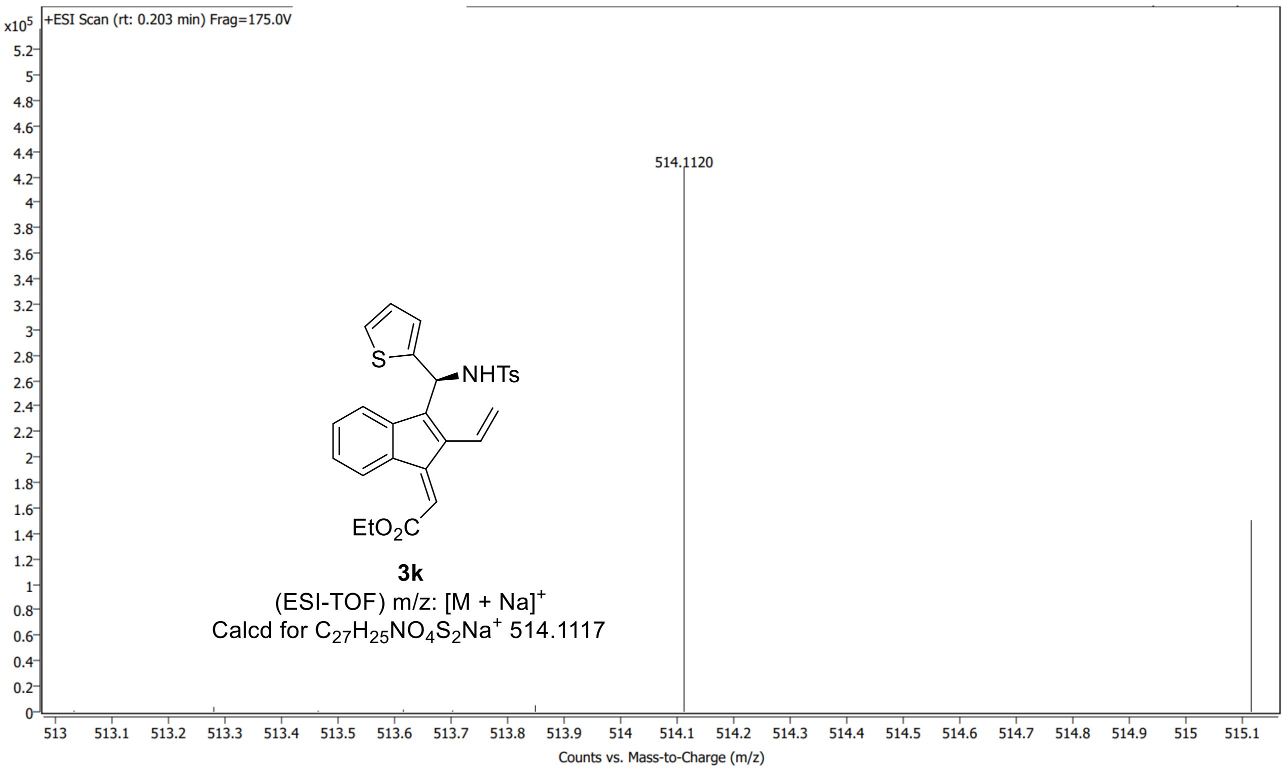
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.290 | BB | 0.28 | 606.4496 | 11087.7090 | 49.7844 |
| 8.543 | BV R | 0.30 | 560.0510 | 11183.7588 | 50.2156 |
| | | | Totals: | 22271.4678 | 100.0000 |



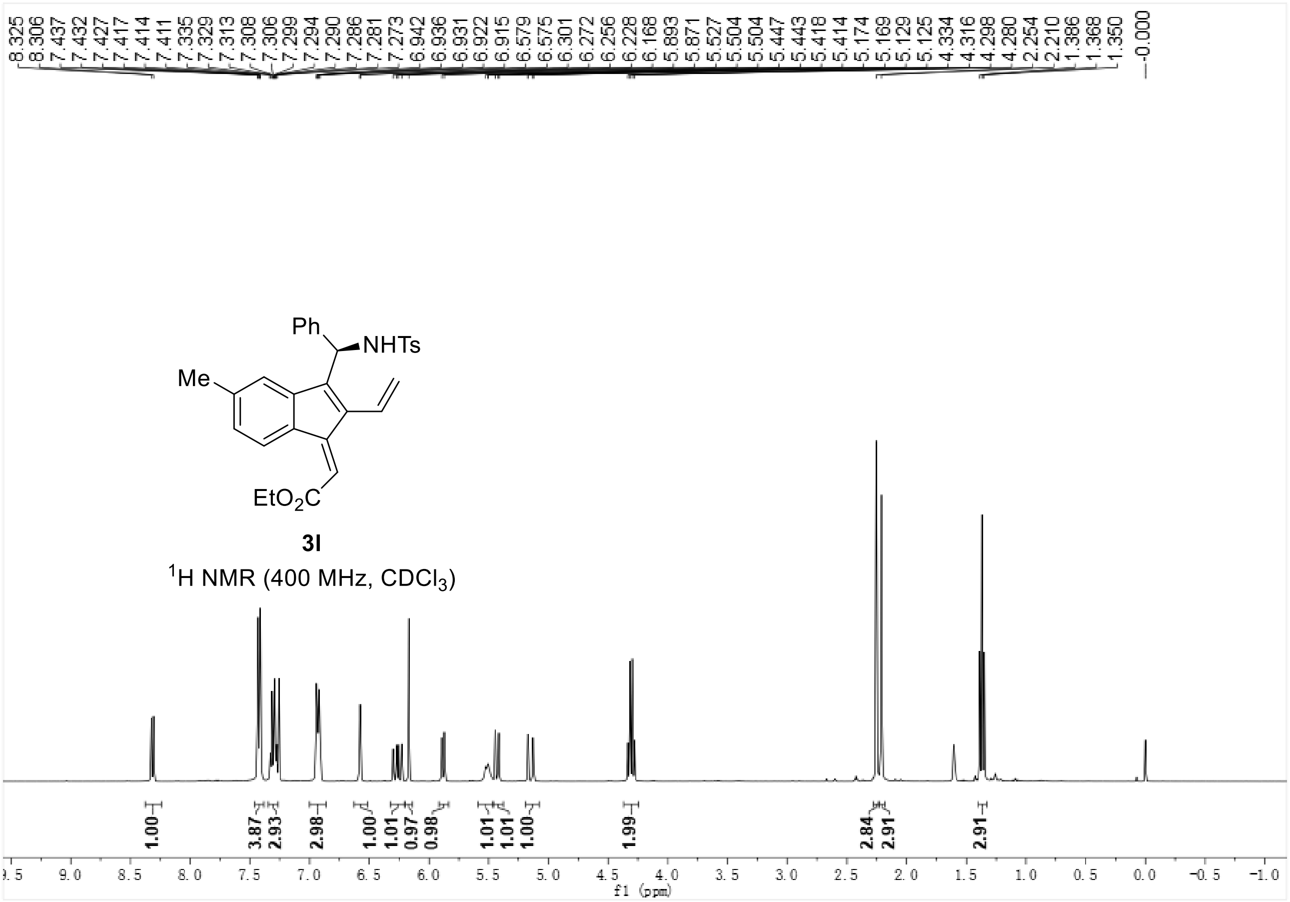
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.311 | BBA | 0.20 | 69.0308 | 897.5580 | 5.8031 |
| 8.575 | BB | 0.24 | 918.9404 | 14569.3174 | 94.1969 |
| | | | Totals: | 15466.8754 | 100.0000 |



**3k**

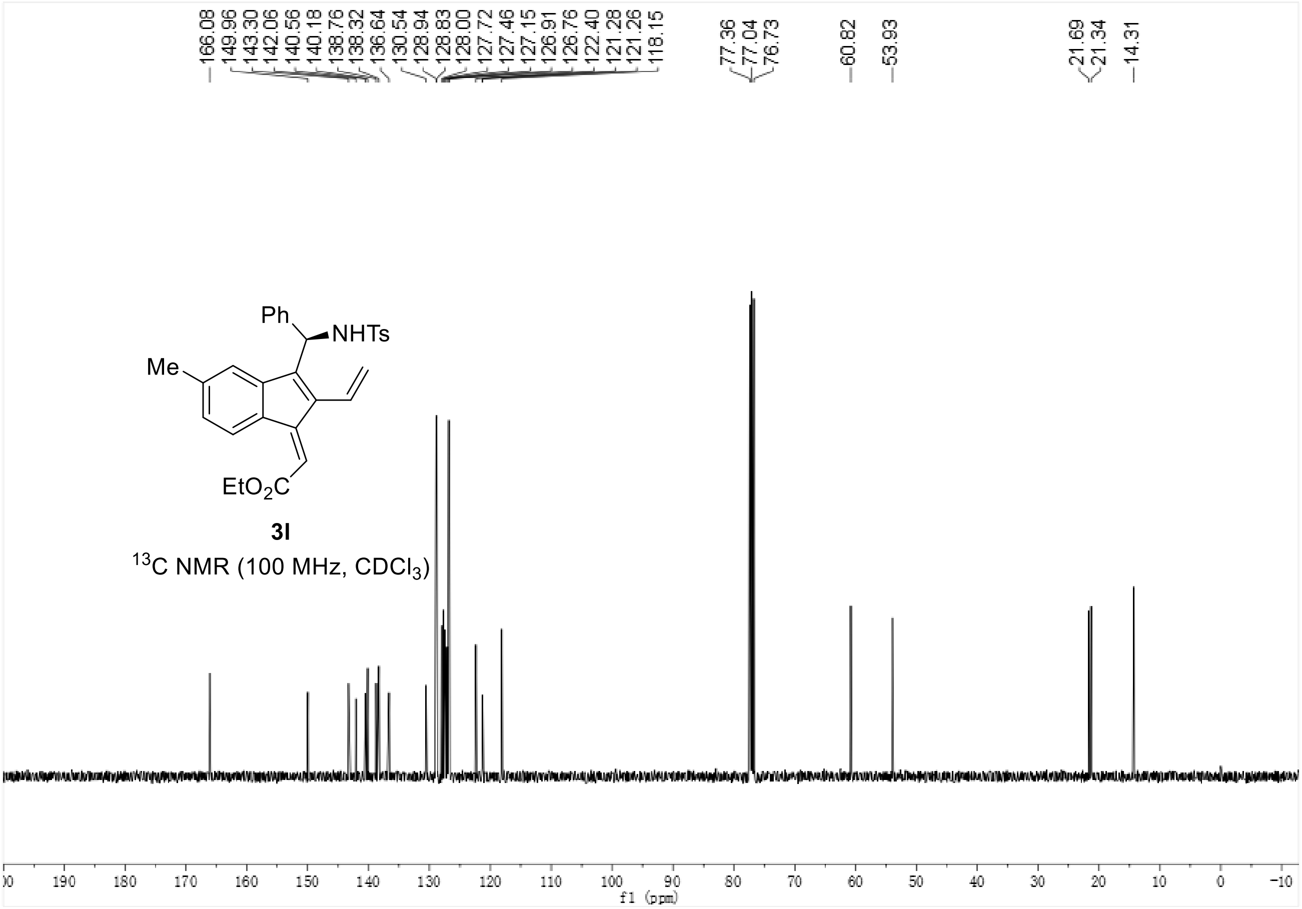
(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{27}H_{25}NO_4S_2Na^+$ 514.1117



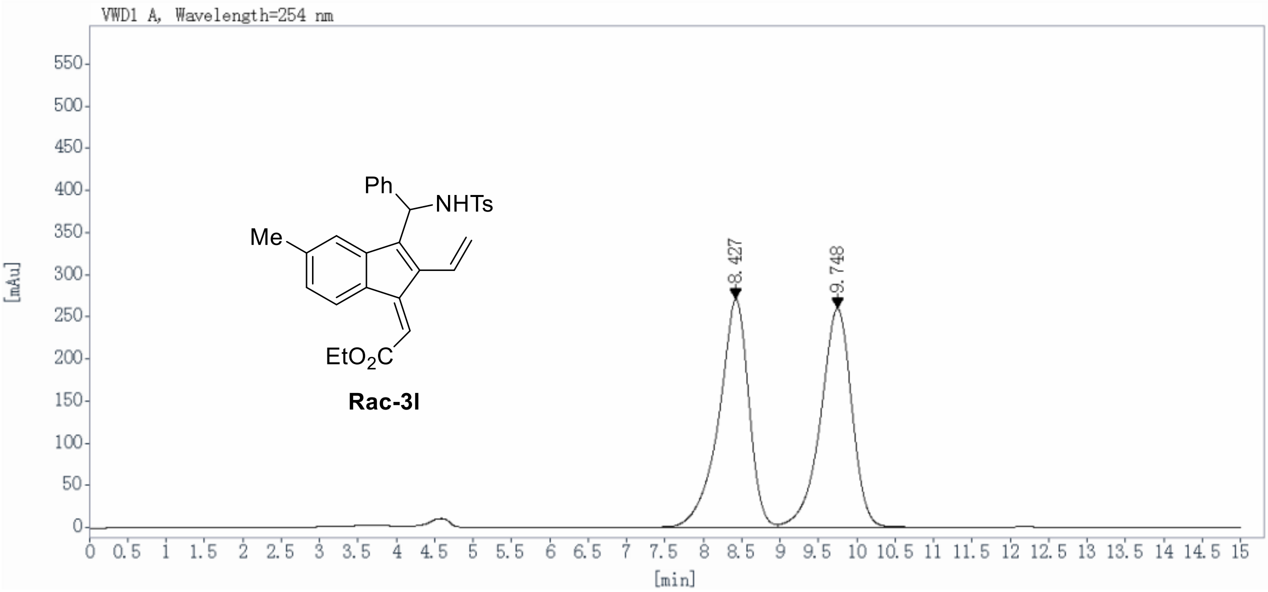
**3l**

$^1$H NMR (400 MHz, CDCl$_3$)

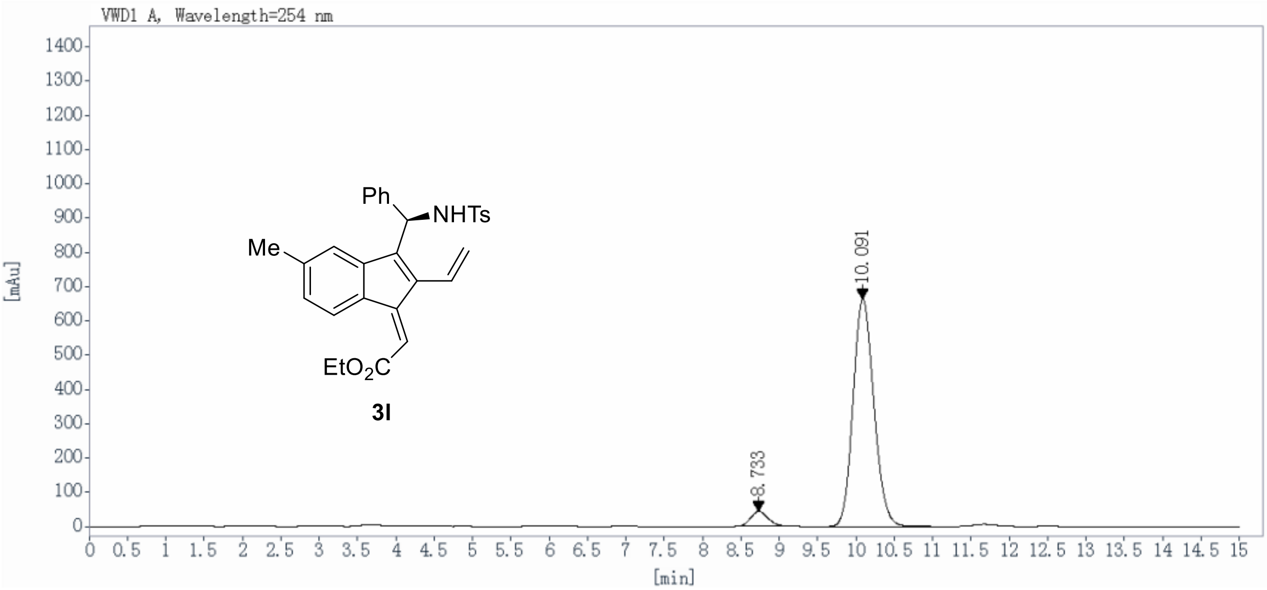


**3l**

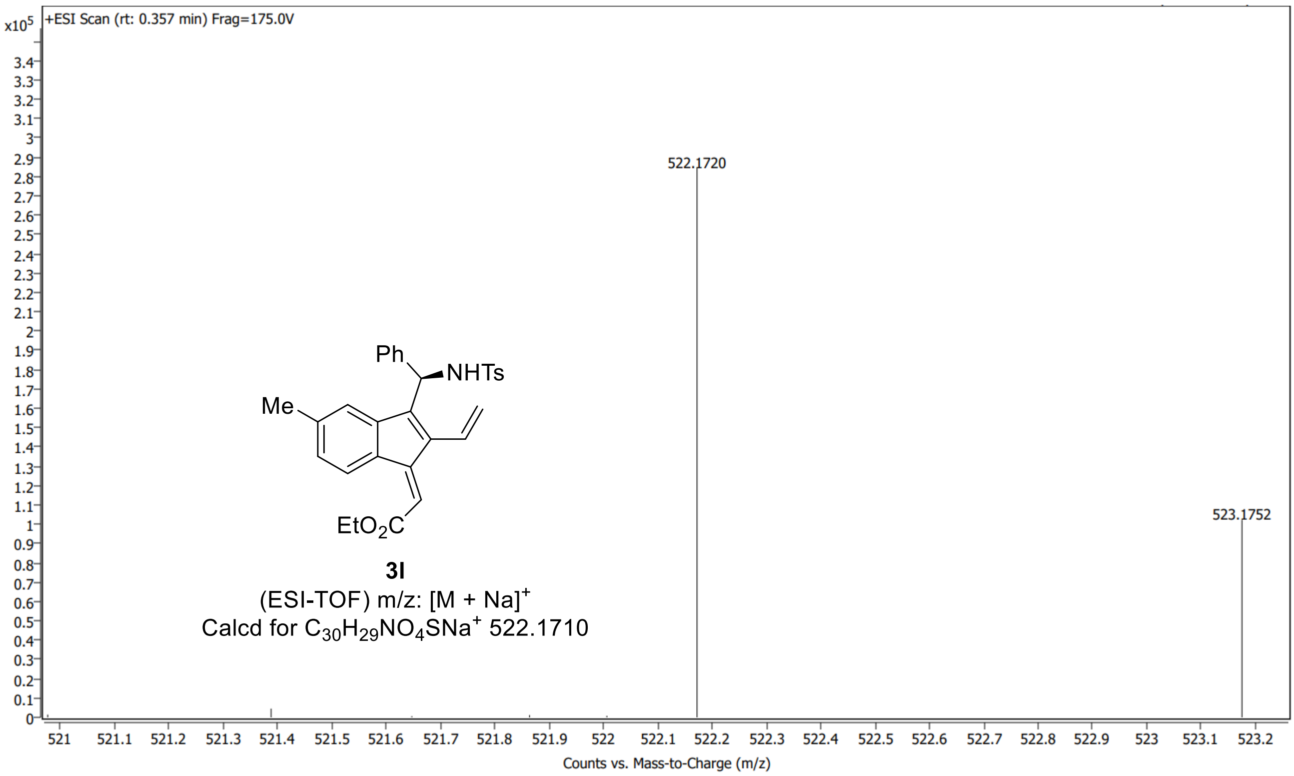
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.427 | BV | 0.40 | 270.6519 | 7366.6909 | 50.0479 |
| 9.748 | VB | 0.43 | 259.5555 | 7352.5889 | 49.9521 |
| | | | Totals: | 14719.2798 | 100.0000 |



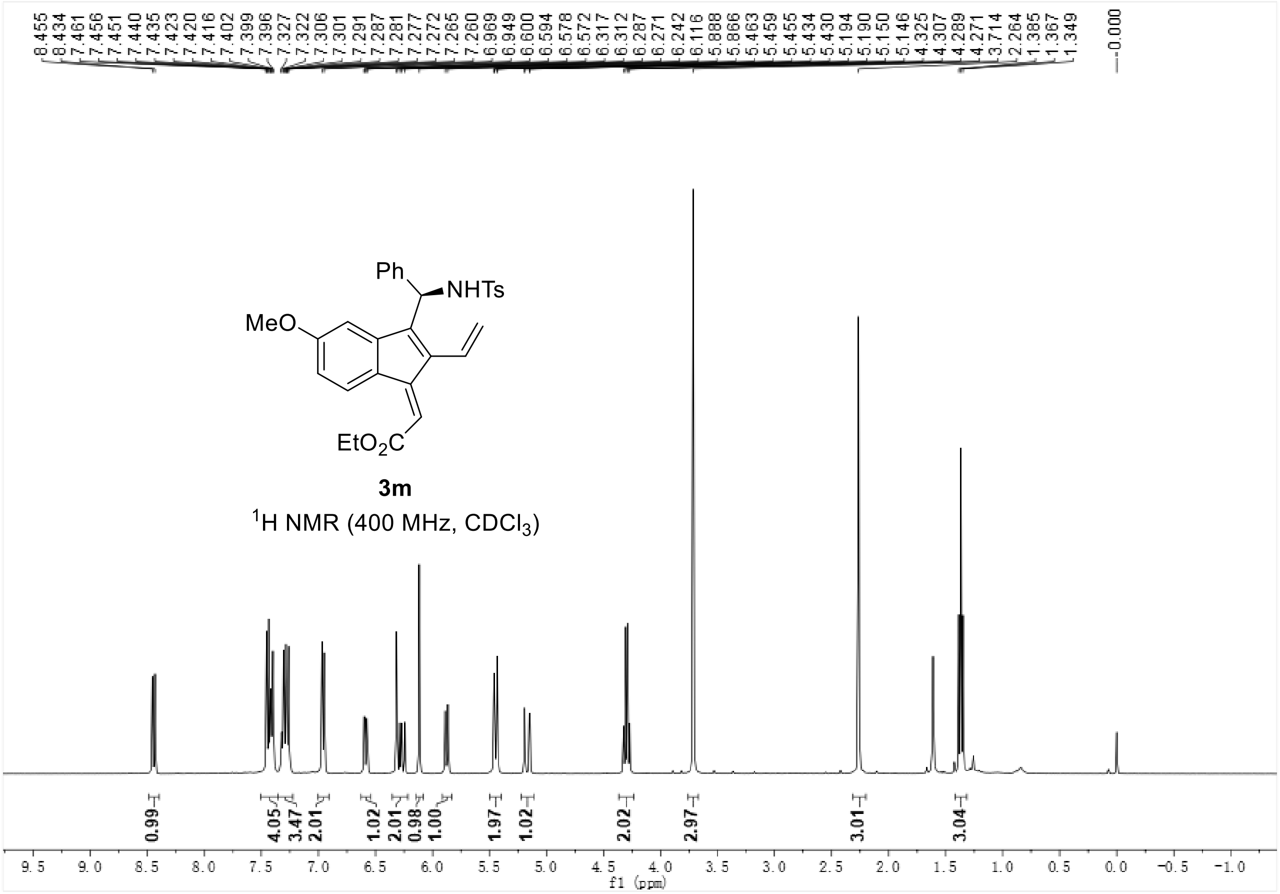
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.733 | BBA | 0.24 | 42.9750 | 669.2707 | 5.0734 |
| 10.091 | BB | 0.29 | 664.4868 | 12522.4707 | 94.9266 |
| | | | Totals: | 13191.7414 | 100.0000 |



**3l**

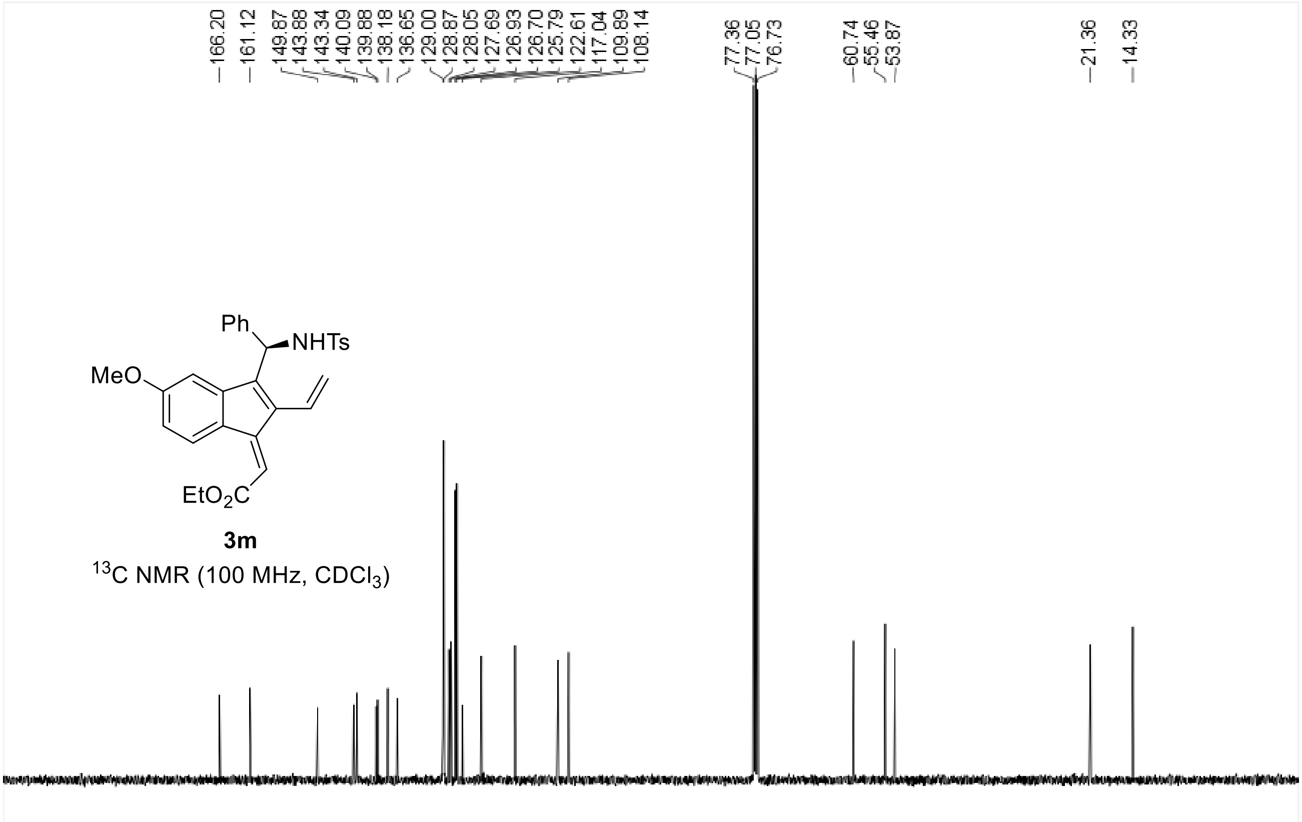
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710



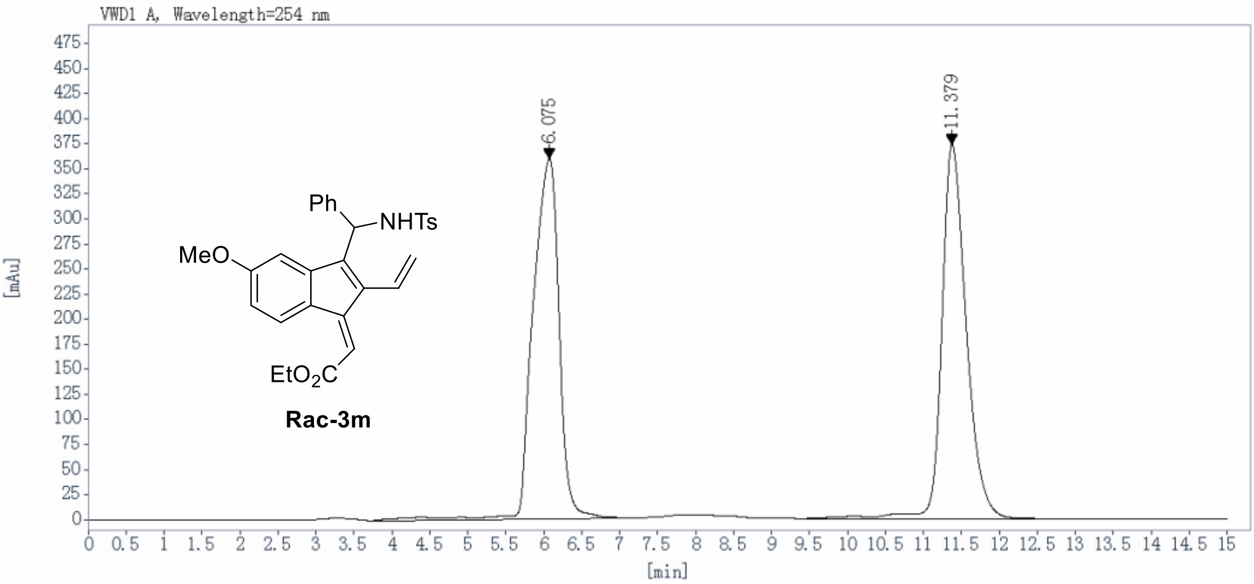
**3m**

$^{1}$H NMR (400 MHz, CDCl$_3$)

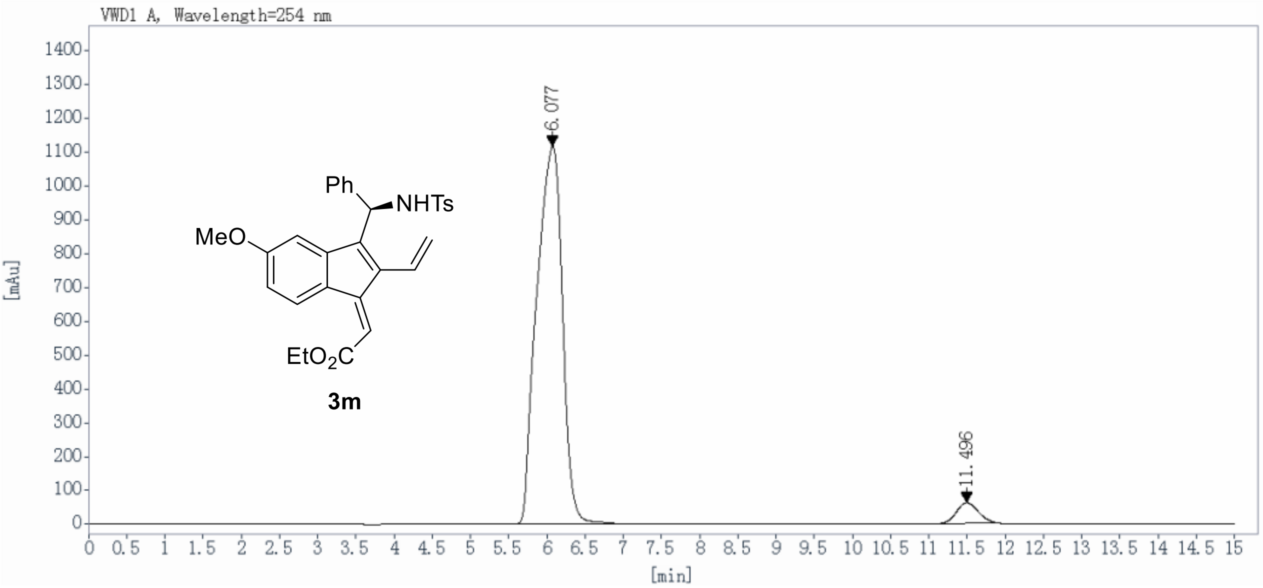


**3m**

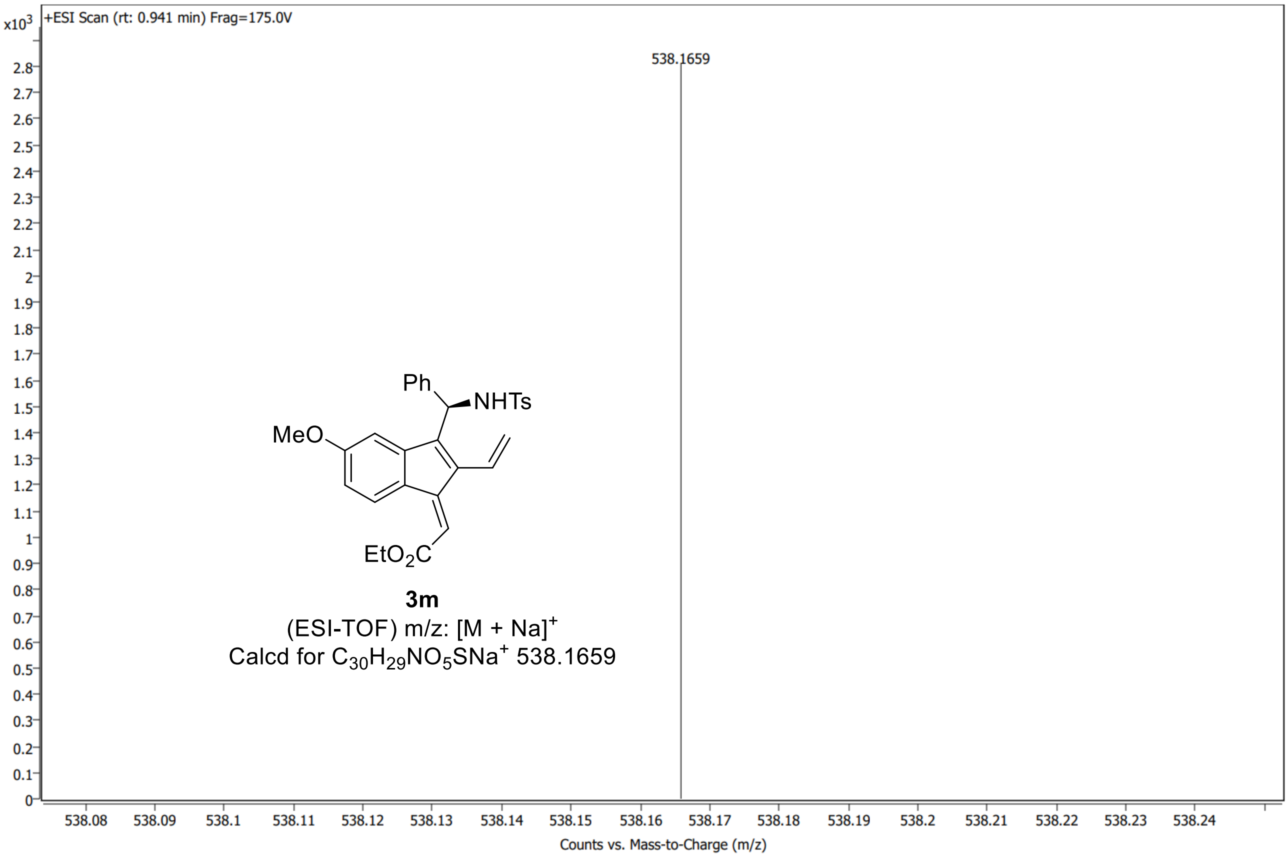
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.075 | VB R | 0.40 | 358.9065 | 8585.2813 | 50.3513 |
| 11.379 | VB R | 0.34 | 373.4622 | 8465.4717 | 49.6487 |
| | | | Totals: | 17050.7529 | 100.0000 |



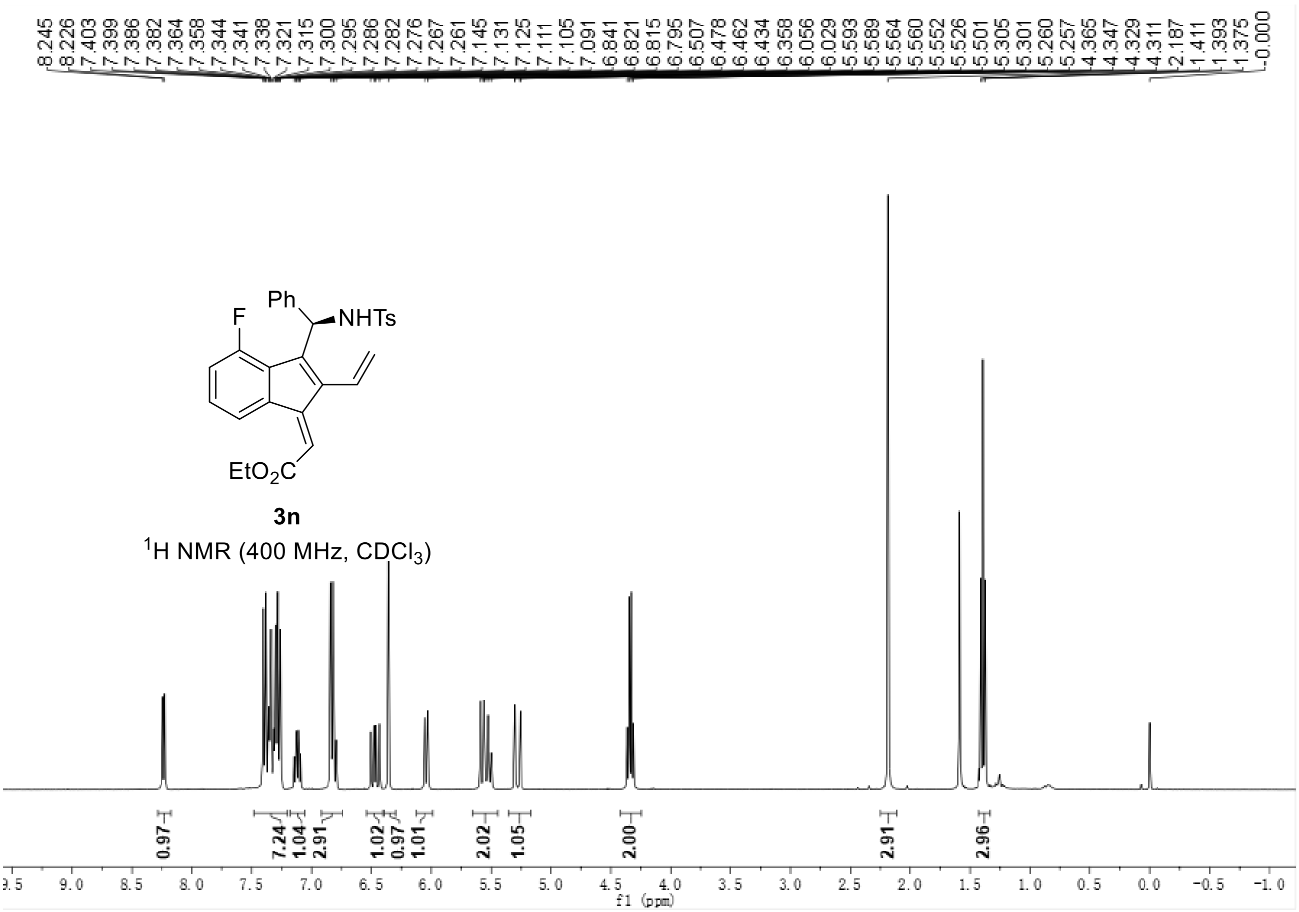
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.077 | BB | 0.36 | 1116.8179 | 26050.5859 | 95.5844 |
| 11.496 | BBA | 0.31 | 60.8612 | 1203.4249 | 4.4156 |
| | | | Totals: | 27254.0109 | 100.0000 |



**3m**

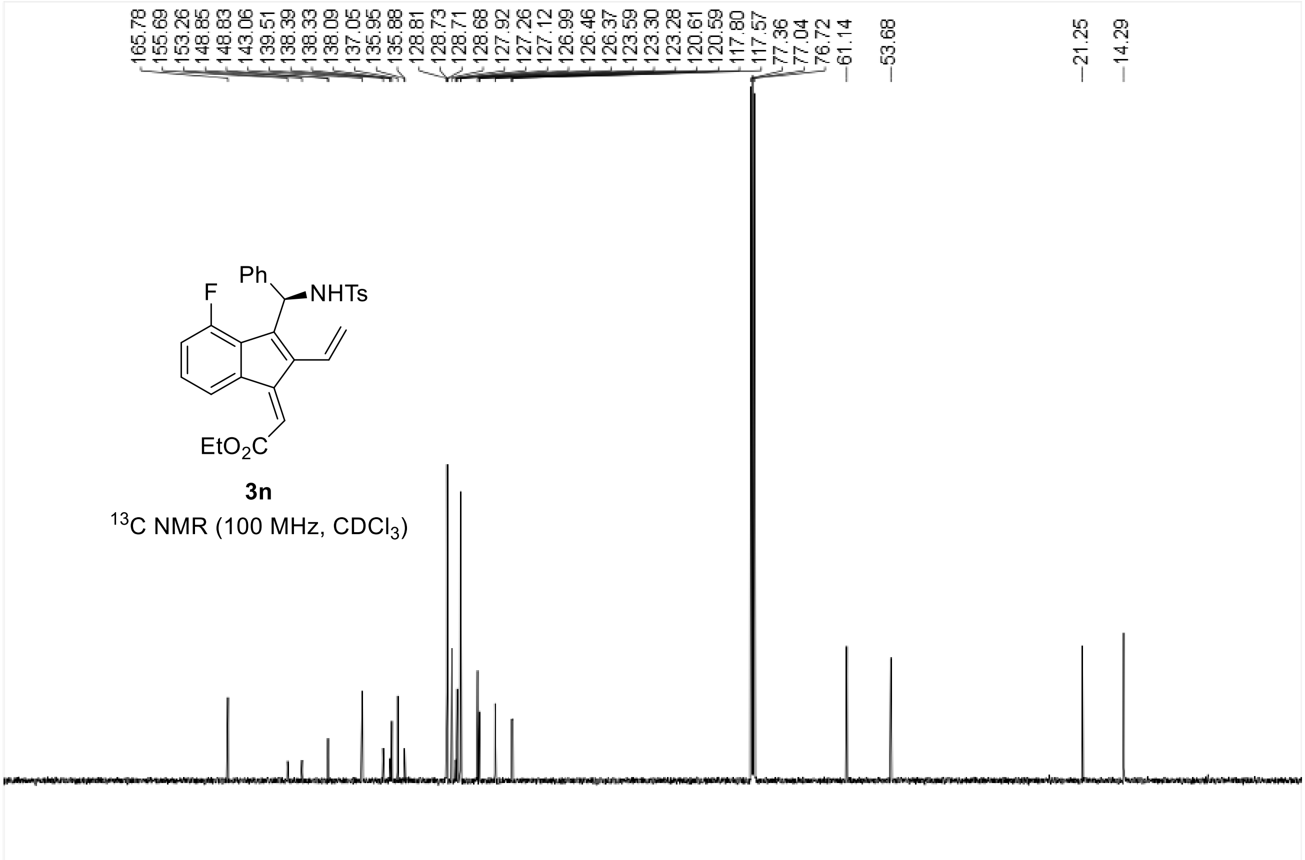
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{29}NO_5SNa^+$ 538.1659



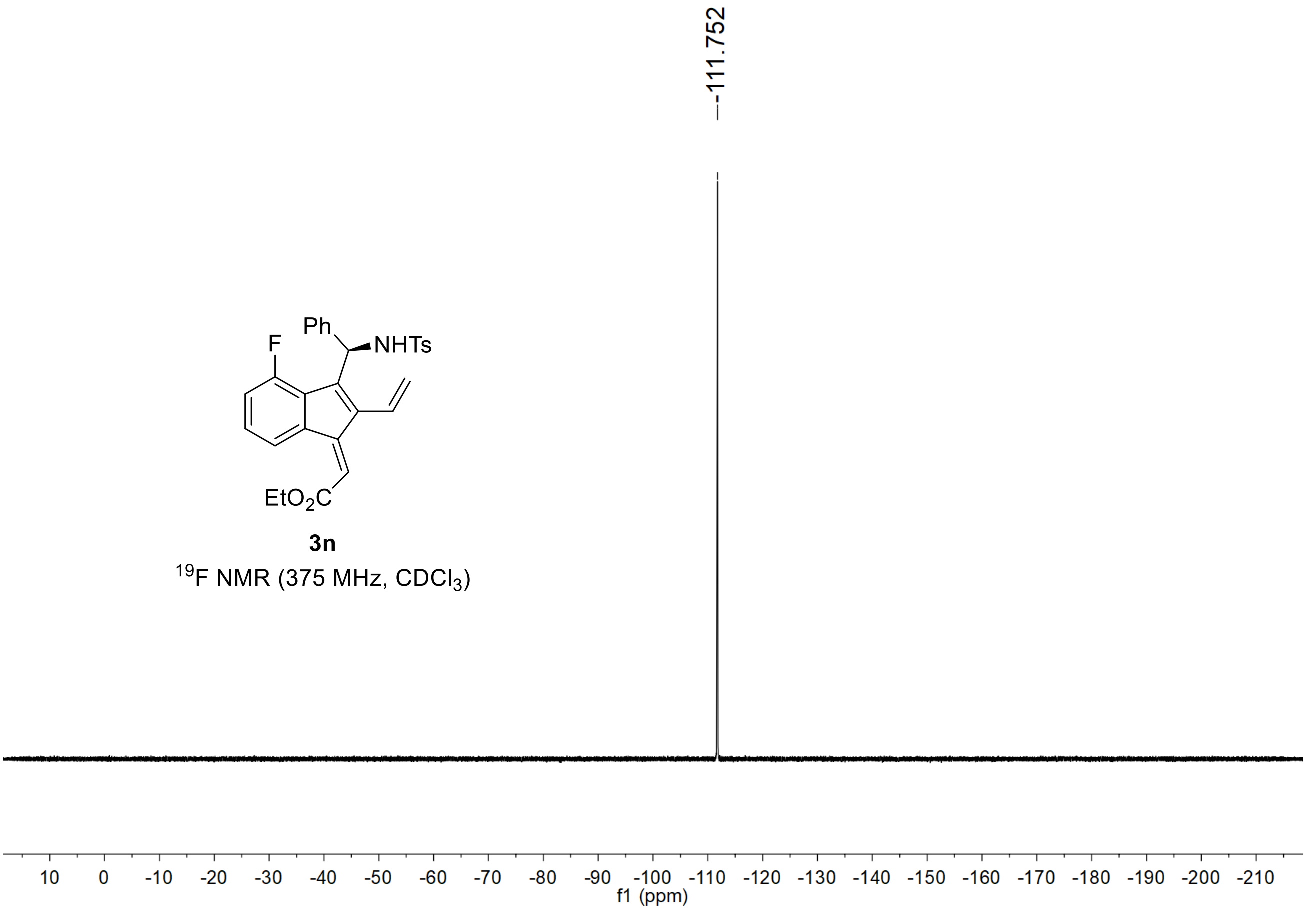
**3n**

$^1$H NMR (400 MHz, CDCl$_3$)



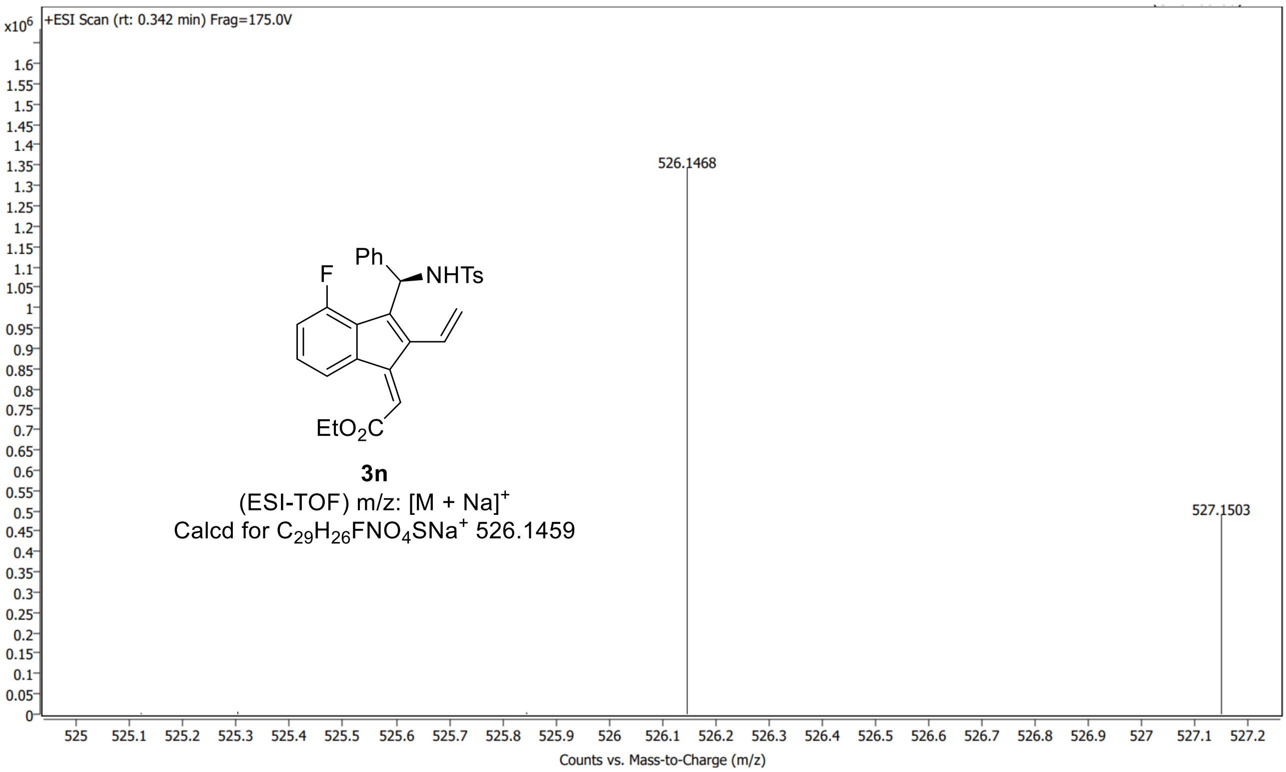
**3n**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**3n**

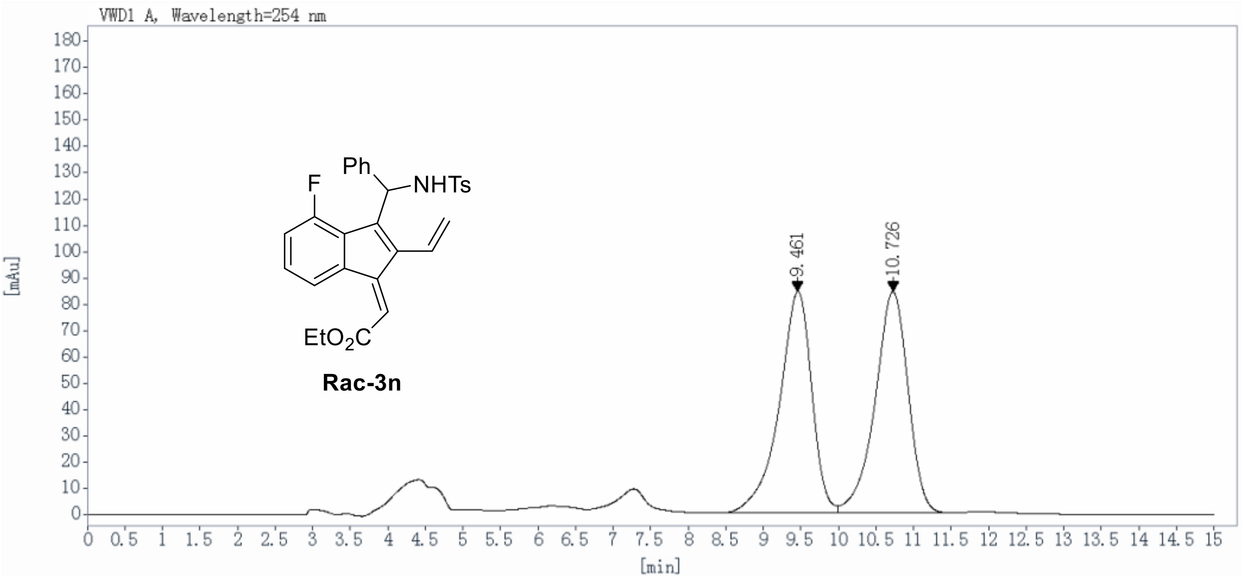
$^{19}$F NMR (375 MHz, $CDCl_3$)



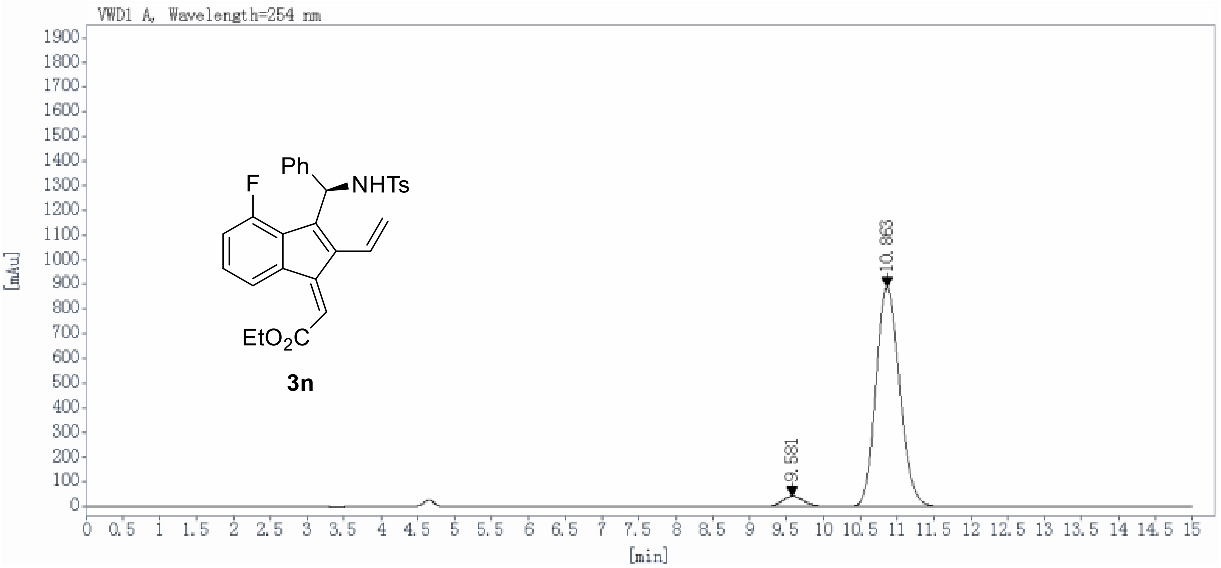
**3n**

(ESI-TOF) m/z: $[M + Na]^+$

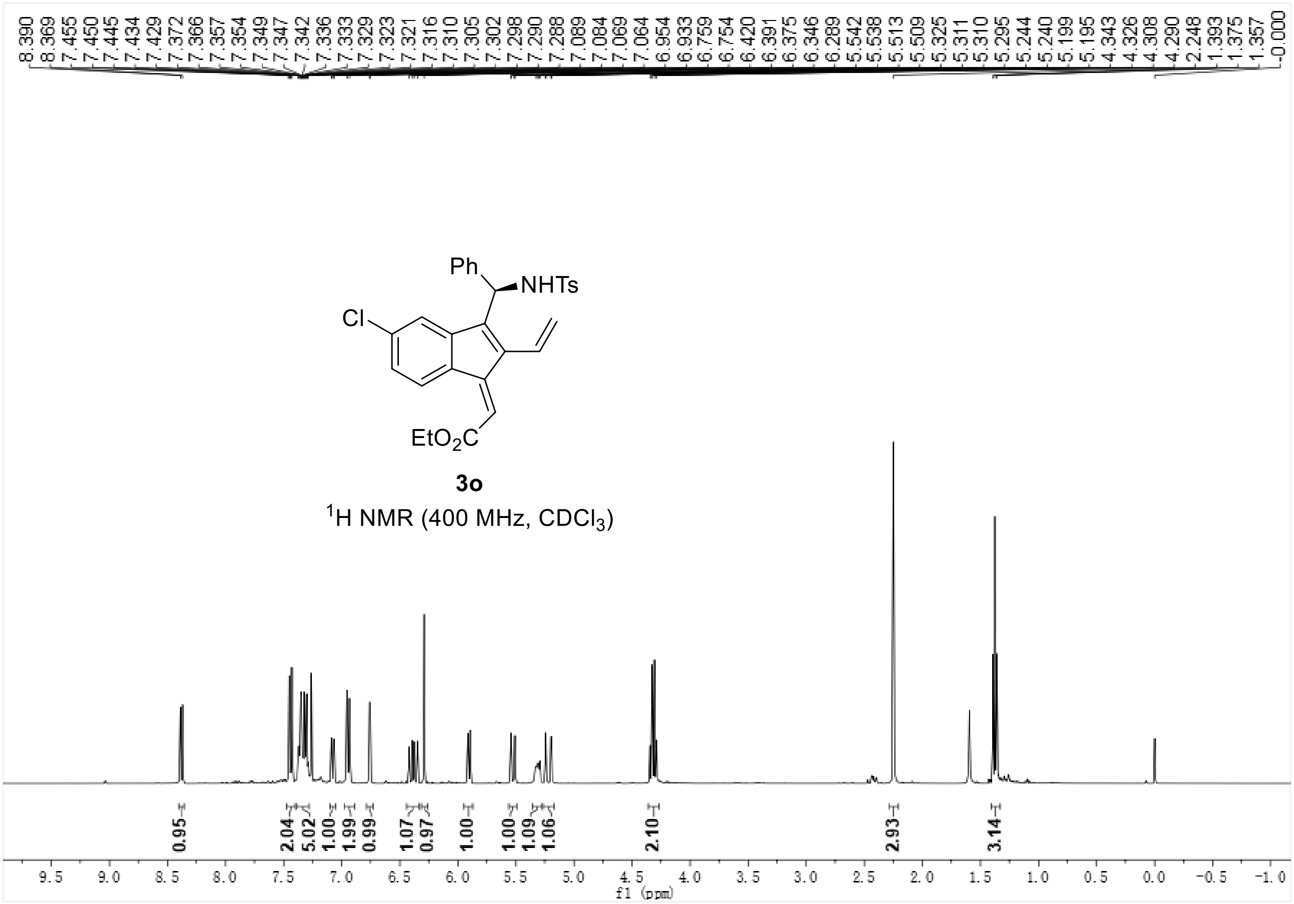
Calcd for $C_{29}H_{26}FNO_4SNa^+$ 526.1459



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.461 | BV | 0.46 | 84.0901 | 2544.9883 | 49.6609 |
| 10.726 | VB | 0.47 | 84.0386 | 2579.7480 | 50.3391 |
| | | | Totals: | 5124.7363 | 100.0000 |

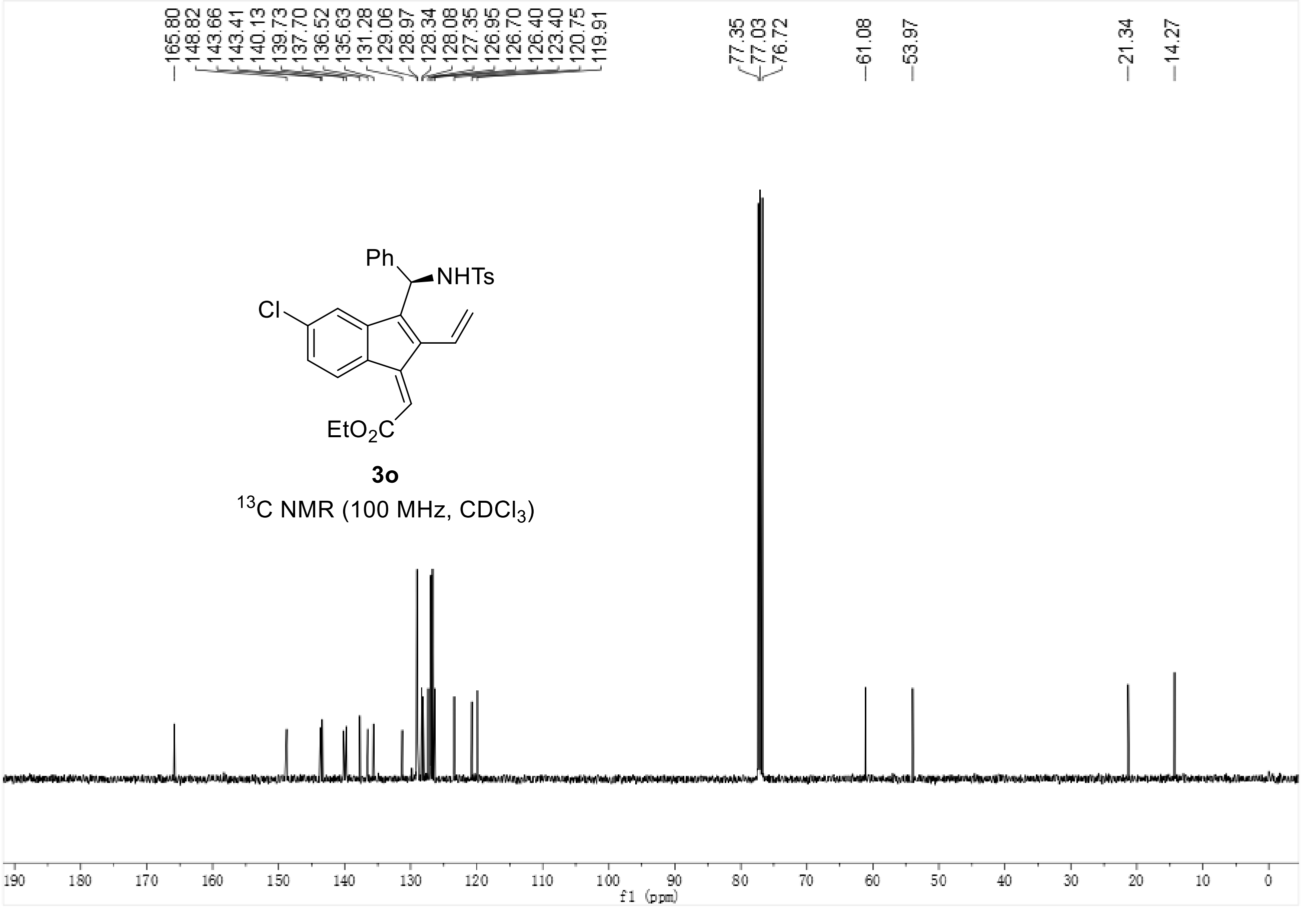


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.581 | BB | 0.32 | 40.4915 | 827.3523 | 4.0005 |
| 10.863 | BB | 0.35 | 887.6186 | 19853.7344 | 95.9995 |
| | | | Totals: | 20681.0867 | 100.0000 |



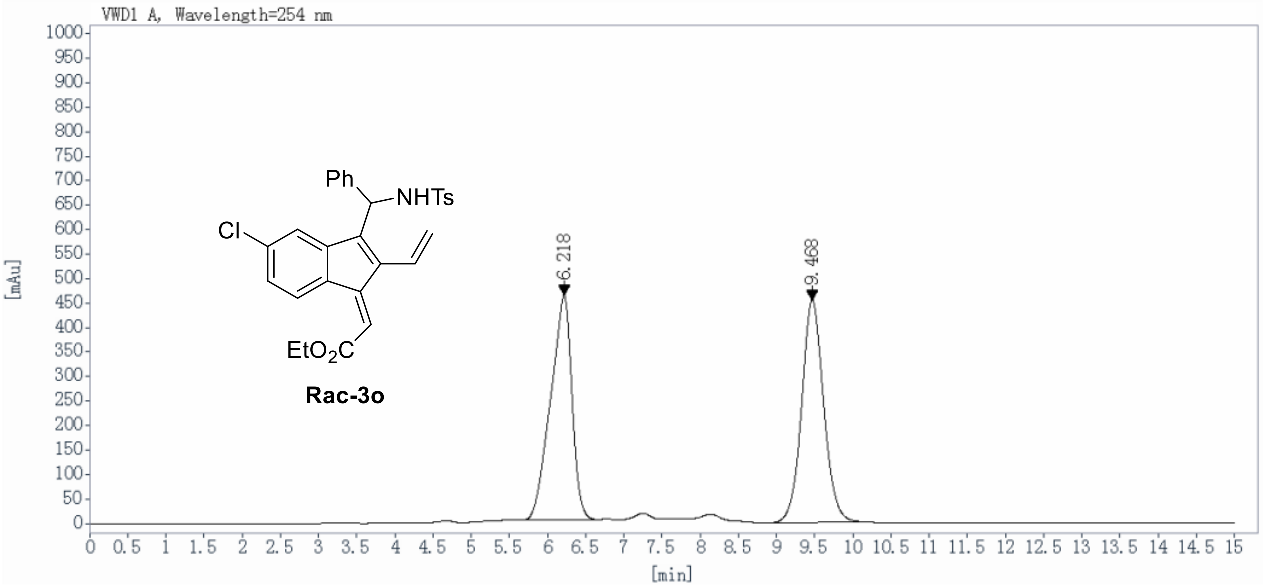
**3o**

$^1$H NMR (400 MHz, CDCl$_3$)

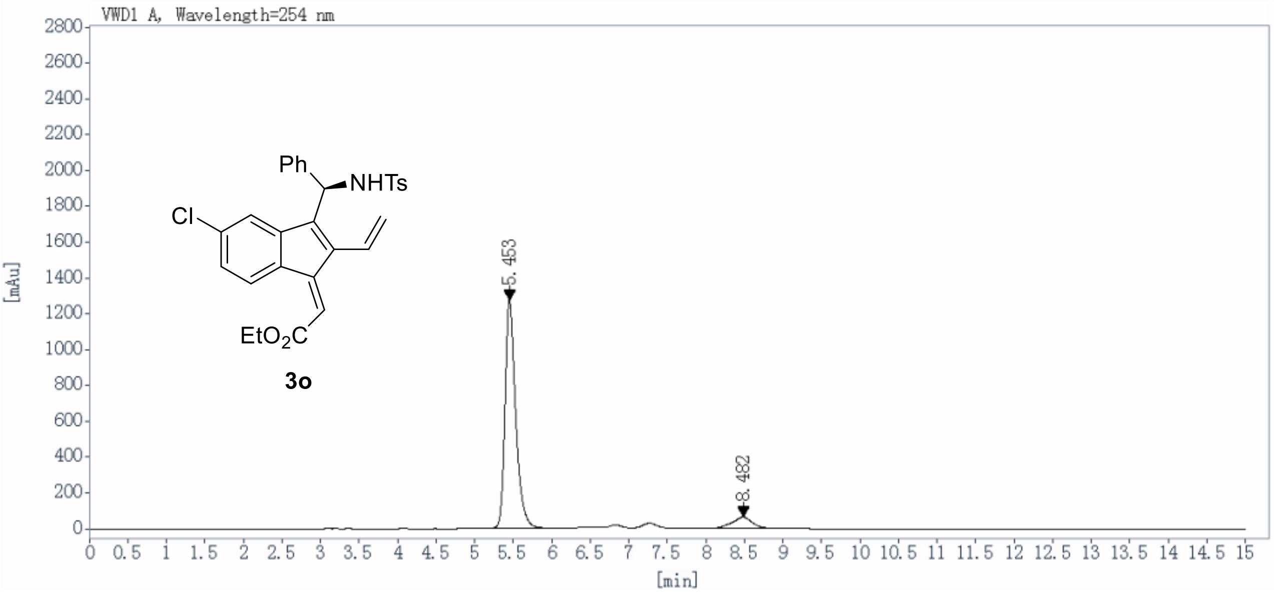


**3o**

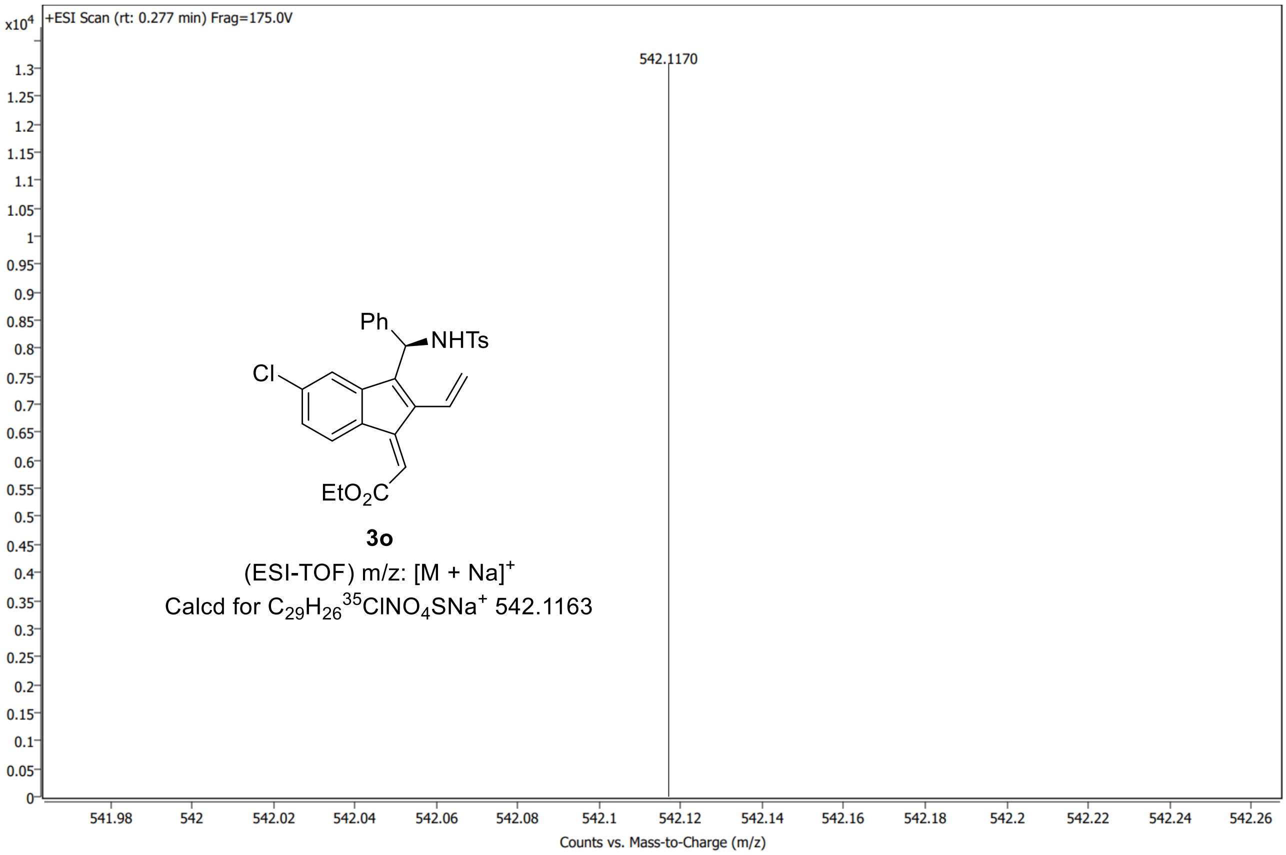
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.218 | VB R | 0.28 | 459.2331 | 8983.3857 | 49.6326 |
| 9.468 | BBA | 0.31 | 454.3322 | 9116.3994 | 50.3674 |
| | | | Totals: | 18099.7852 | 100.0000 |



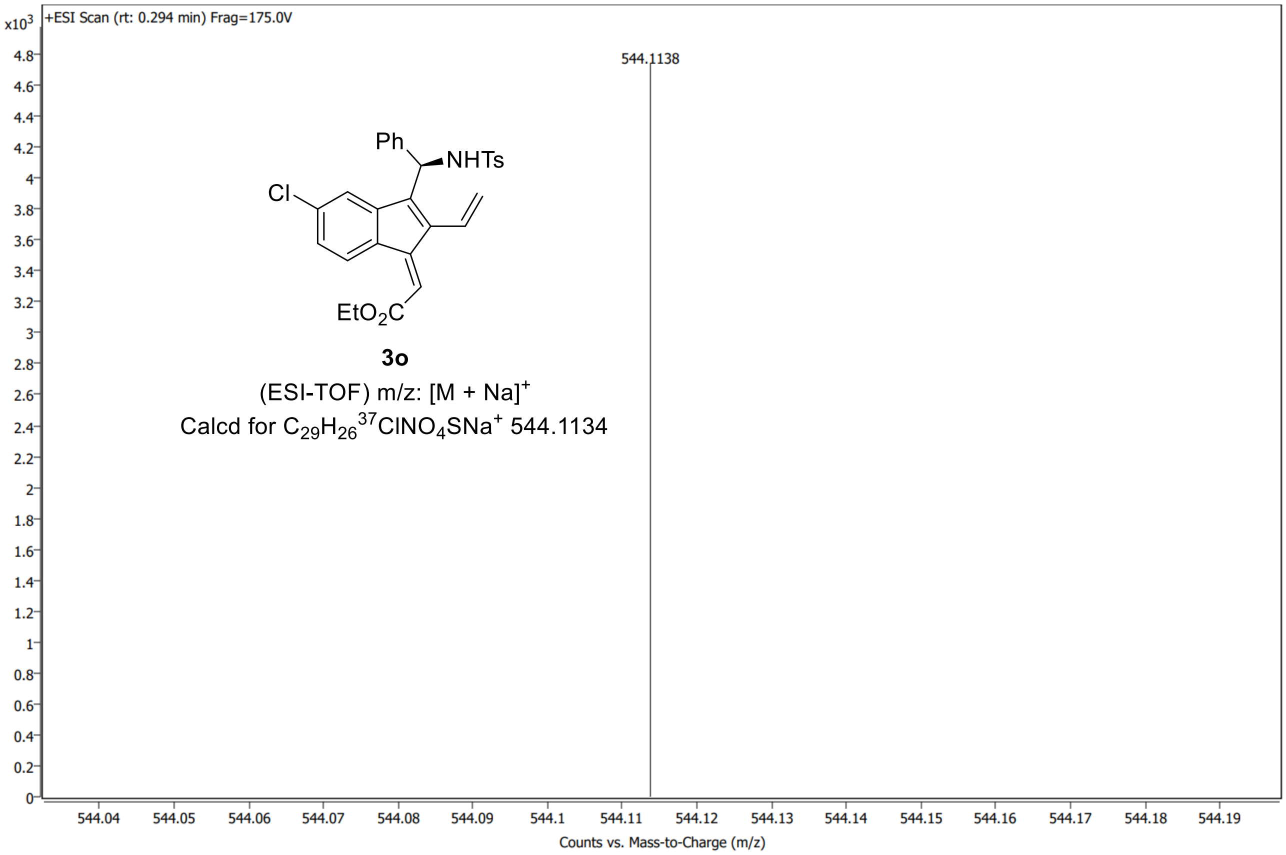
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.453 | BBA | 0.15 | 1278.1001 | 12514.2422 | 91.8596 |
| 8.482 | BBA | 0.26 | 62.5954 | 1108.9912 | 8.1404 |
| | | | Totals: | 13623.2334 | 100.0000 |



**3o**

(ESI-TOF) m/z: $[M + Na]^+$

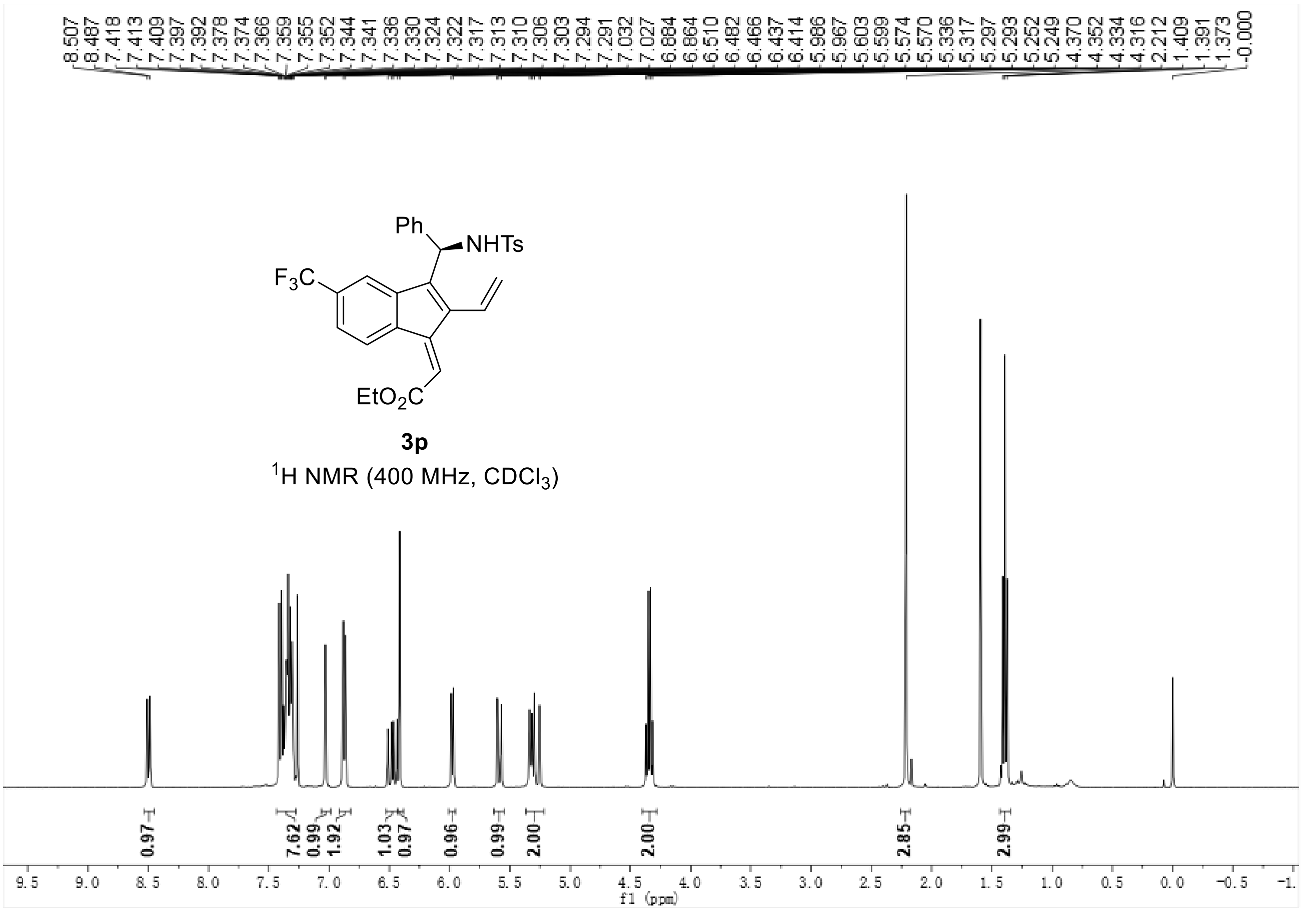
Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163



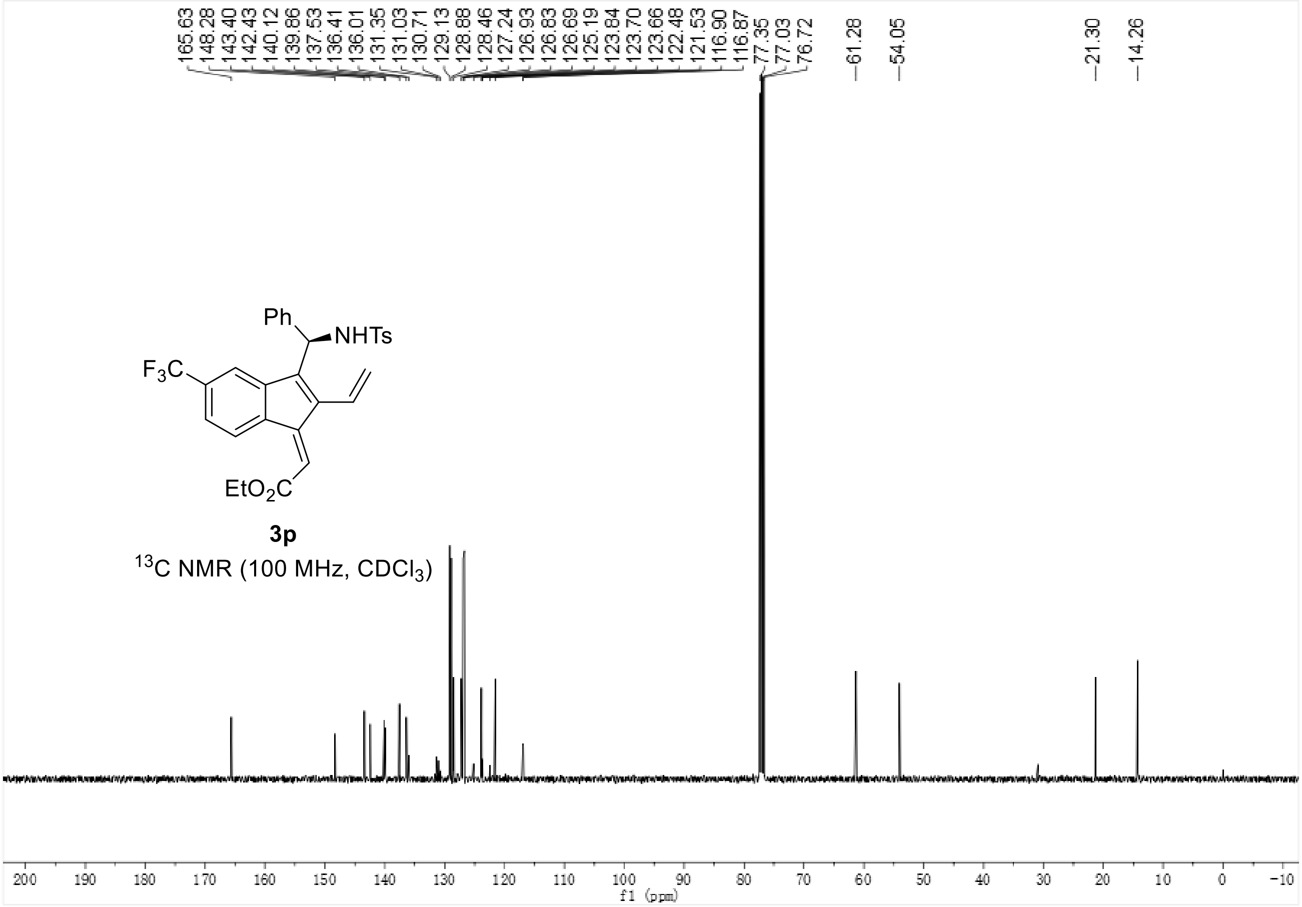
**3o**

(ESI-TOF) m/z: $[M + Na]^+$

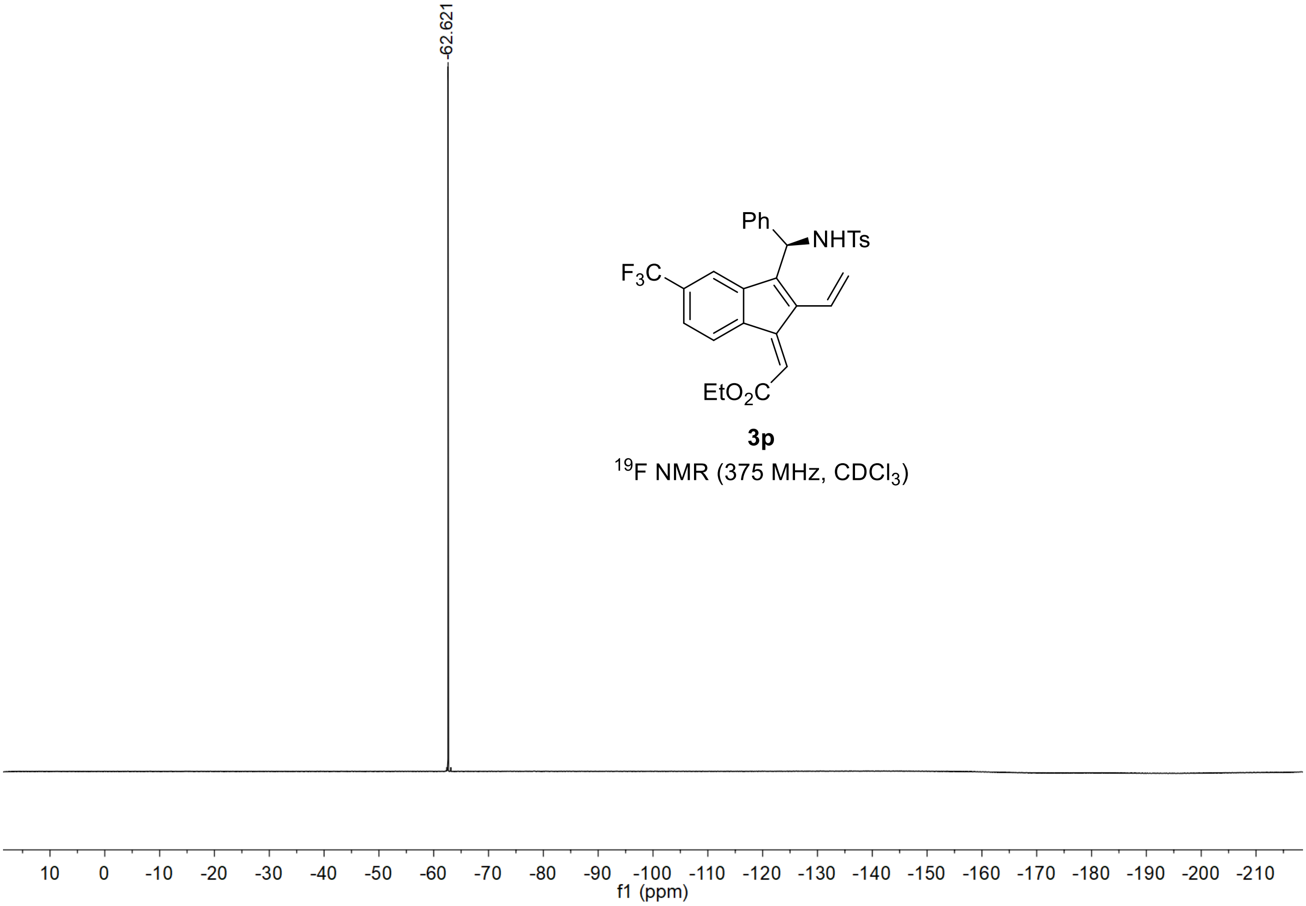
Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134


3p

$^{1}H$ NMR (400 MHz, $CDCl_3$)

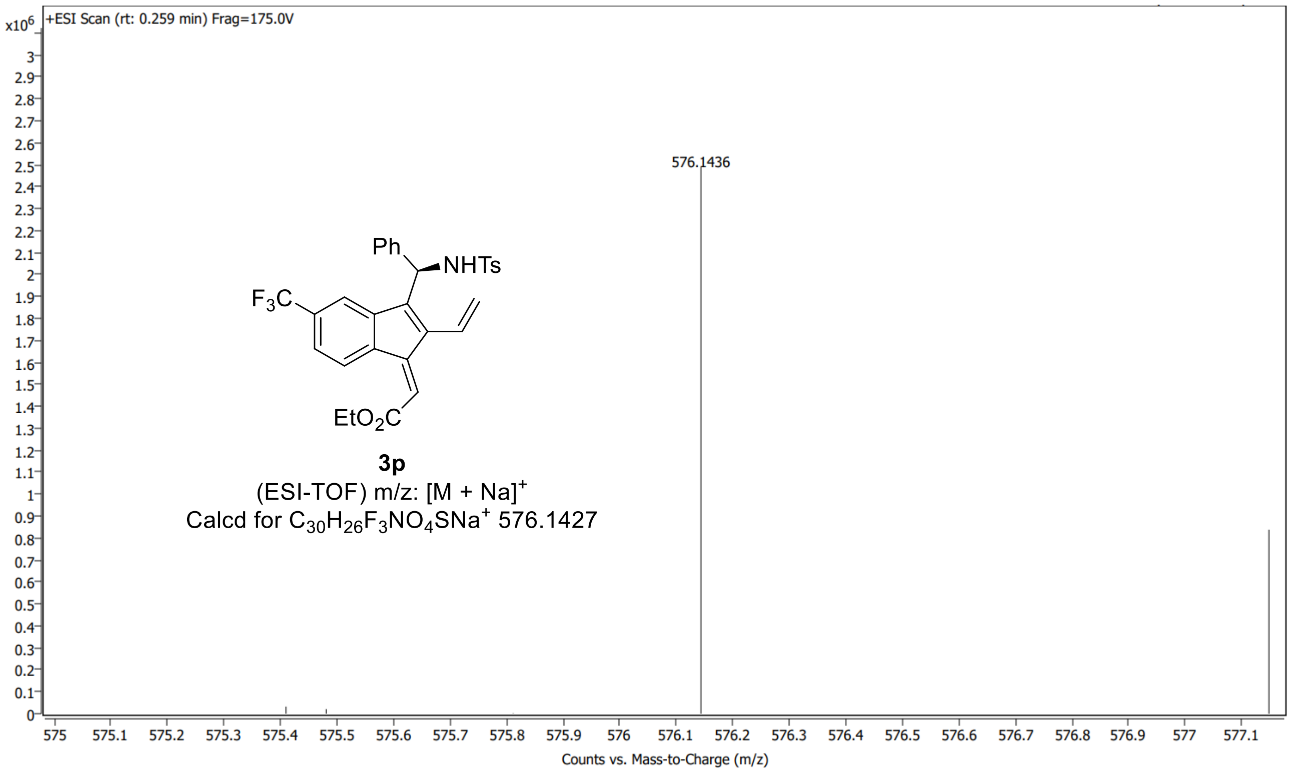

3p

$^{13}C$ NMR (100 MHz, $CDCl_3$)



**3p**

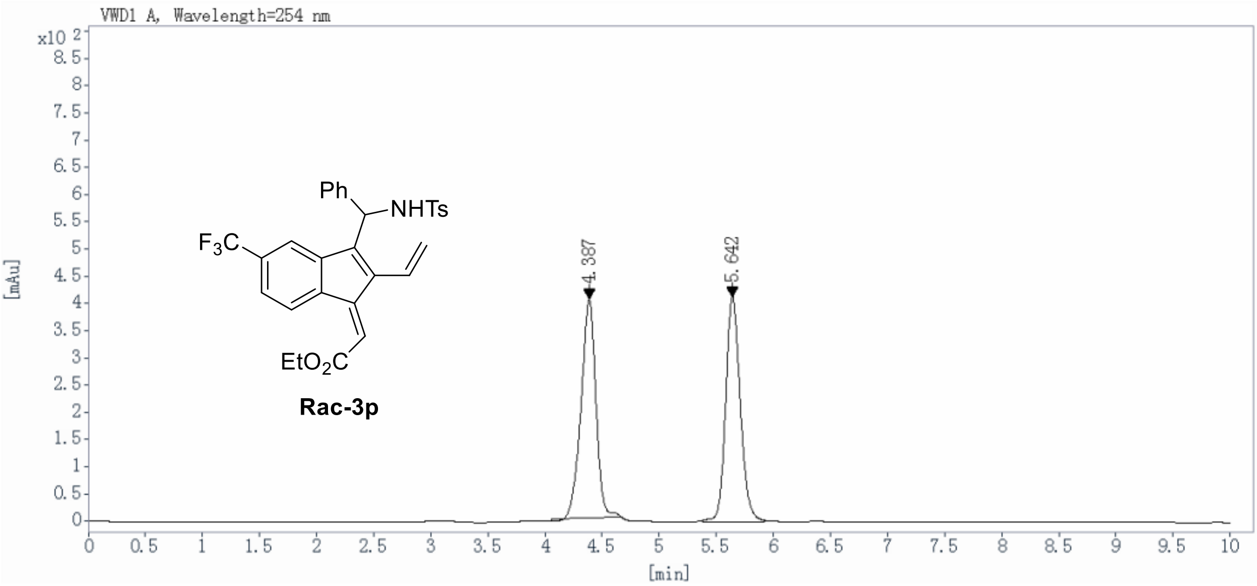
$^{19}$F NMR (375 MHz, $CDCl_3$)



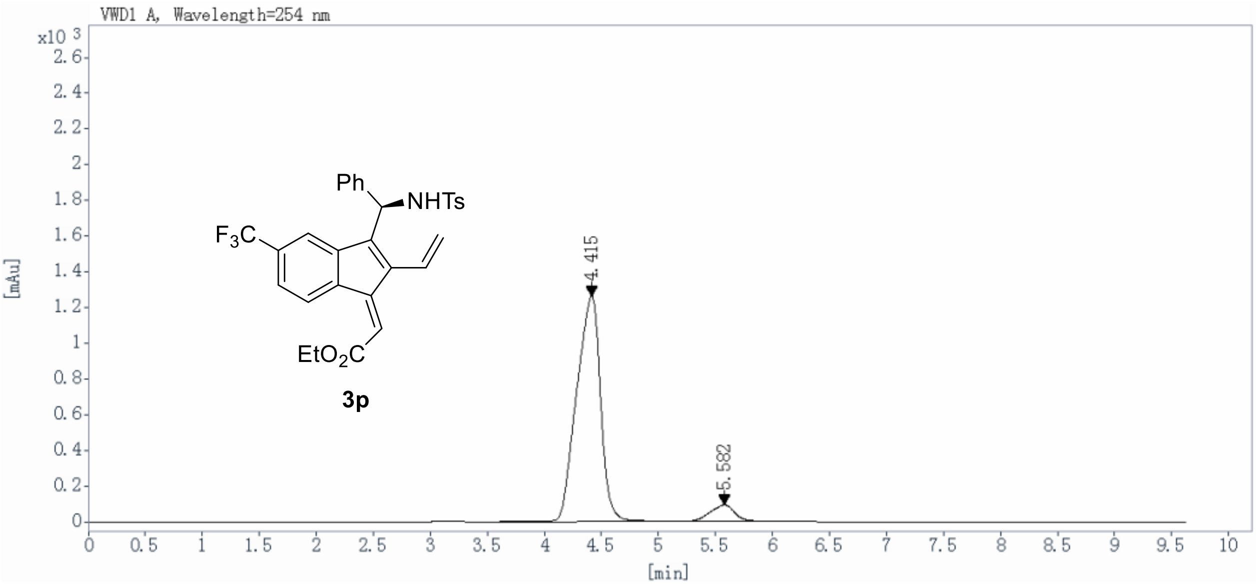
**3p**

(ESI-TOF) m/z: $[M + Na]^+$

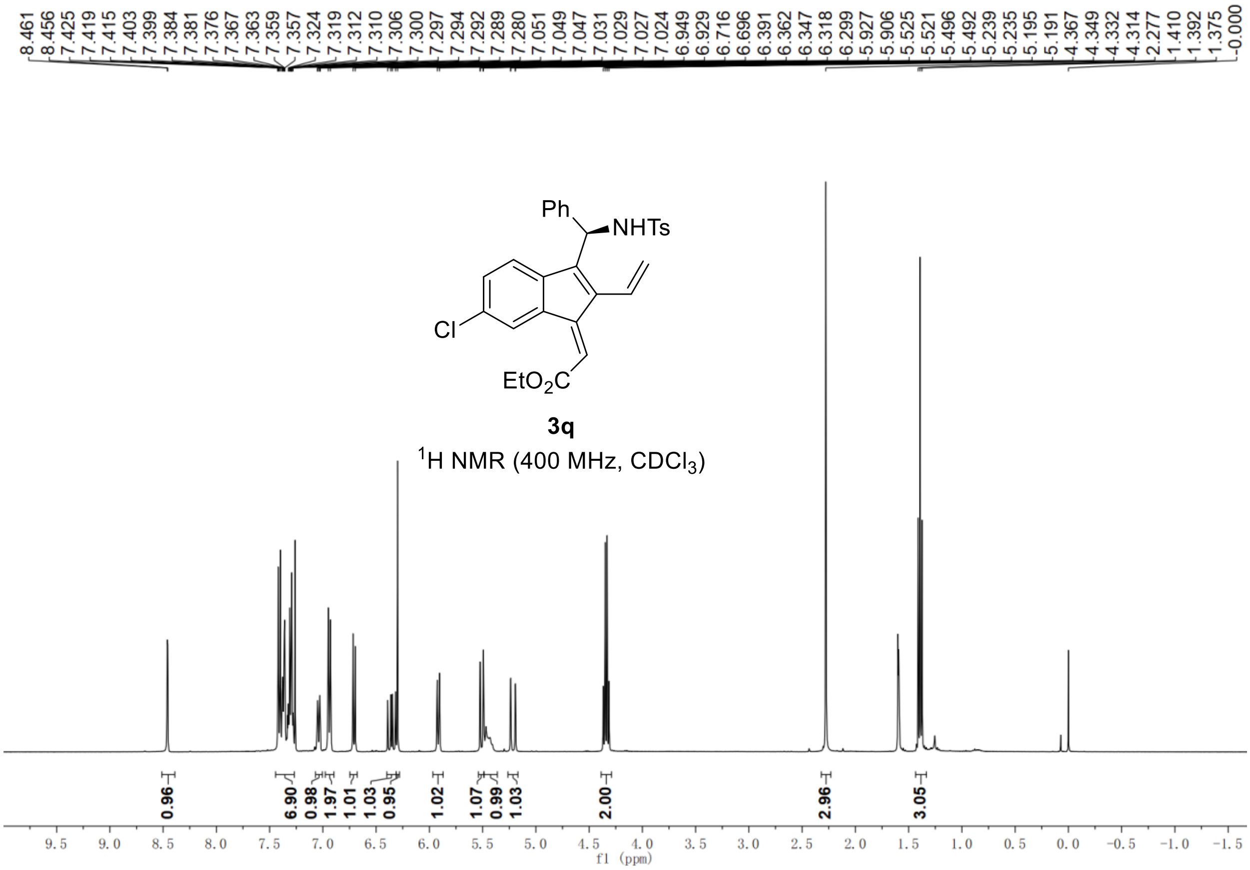
Calcd for $C_{30}H_{26}F_3NO_4SNa^+$ 576.1427



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 4.387 | MM | 0.15 | 401.4993 | 3648.7864 | 49.7731 |
| 5.642 | MM | 0.15 | 413.4528 | 3682.0486 | 50.2269 |
| | | | Totals: | 7330.8350 | 100.0000 |

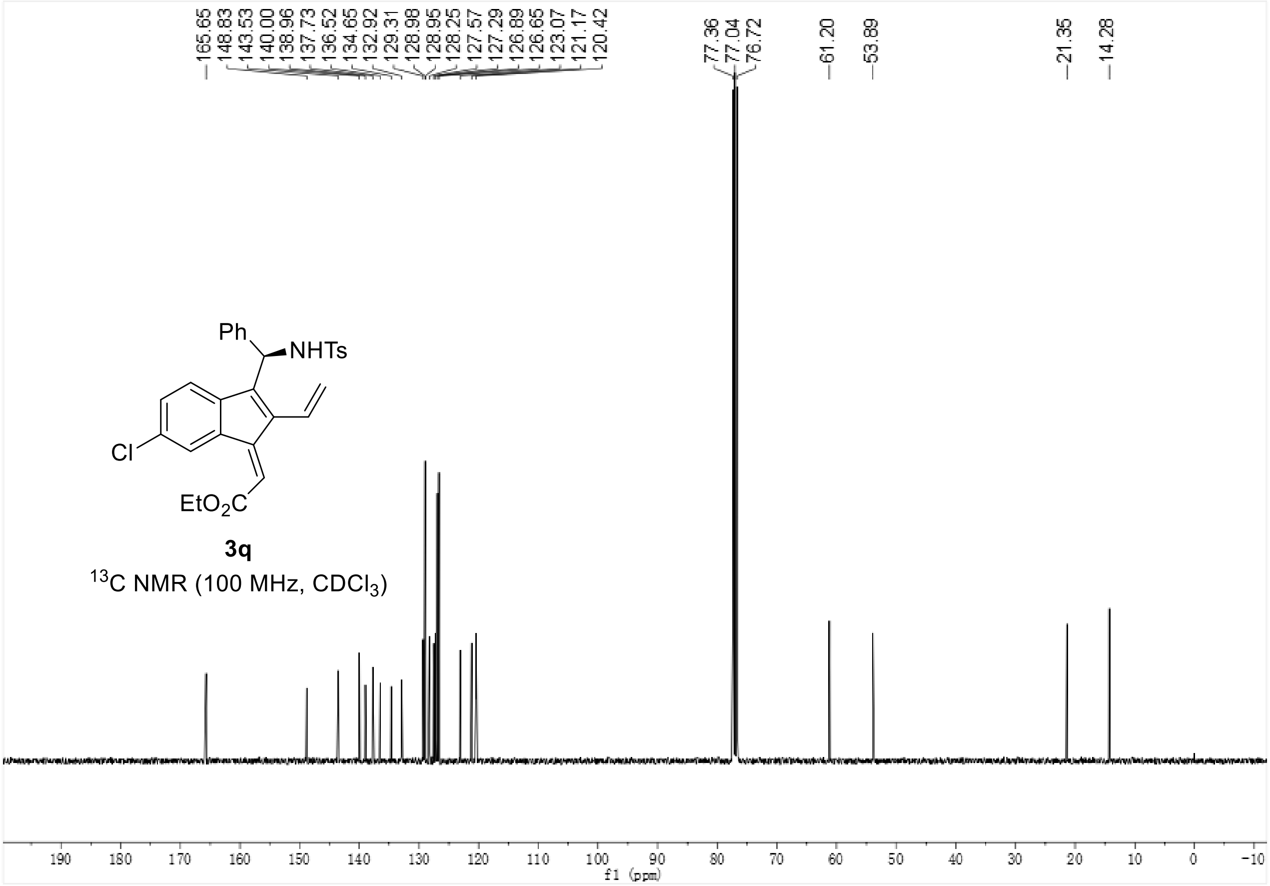


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 4.415 | BBA | 0.24 | 1263.8967 | 18512.2559 | 93.0064 |
| 5.582 | BBA | 0.24 | 92.1169 | 1392.0337 | 6.9936 |
| | | | Totals: | 19904.2896 | 100.0000 |



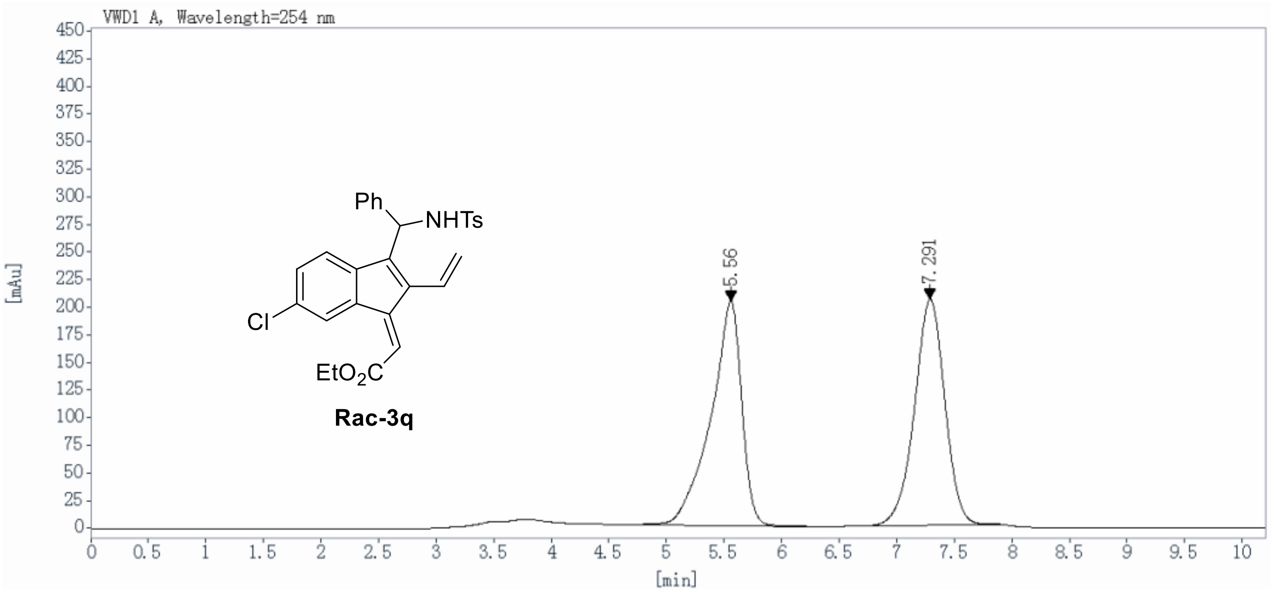
**3q**

$^1$H NMR (400 MHz, $CDCl_3$)

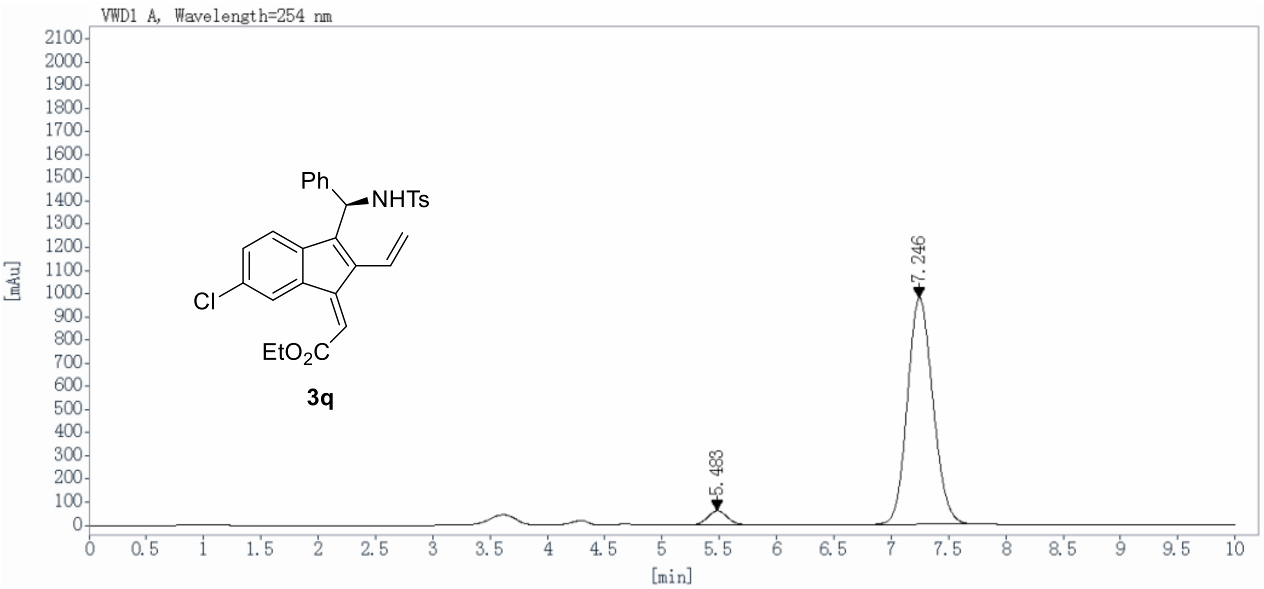


**3q**

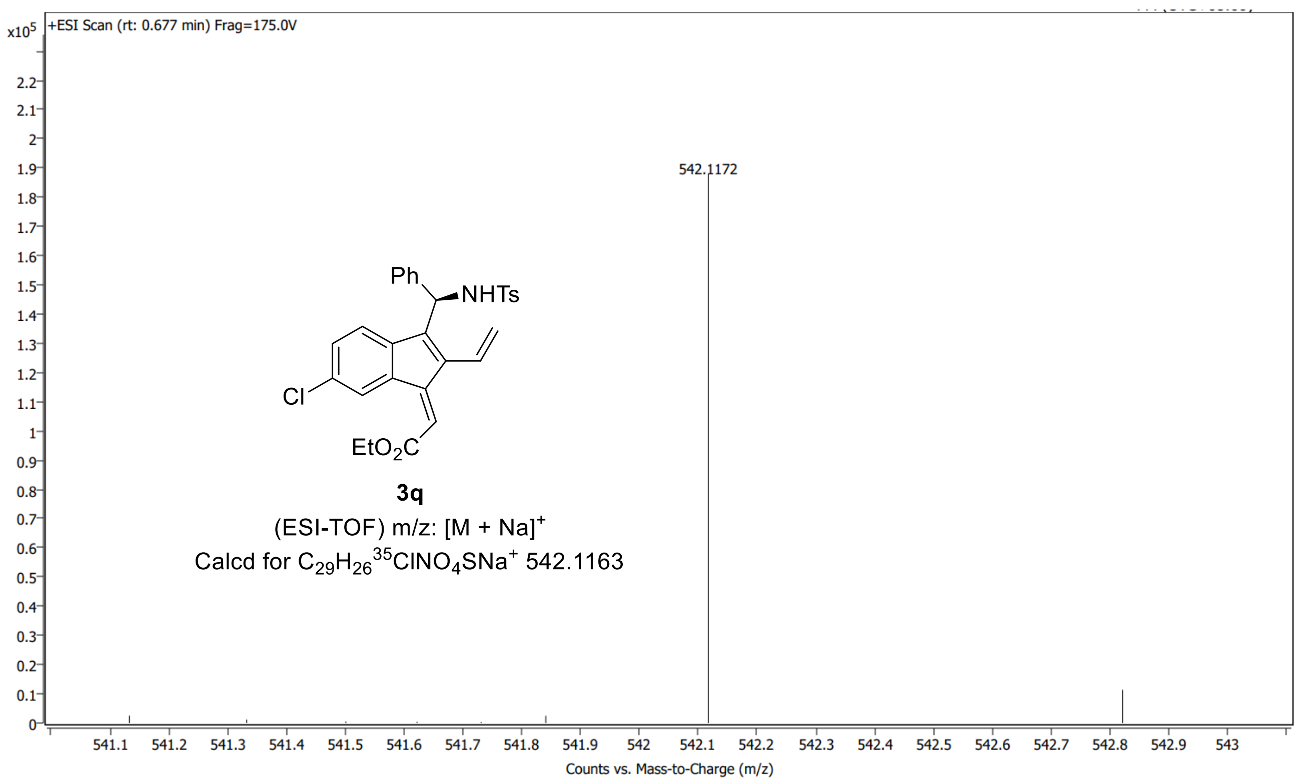
$^{13}$C NMR (100 MHz, $CDCl_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.560 | BBA | 0.26 | 203.4204 | 3787.6702 | 50.0238 |
| 7.291 | BBA | 0.28 | 204.6914 | 3784.0591 | 49.9762 |
| | | | Totals: | 7571.7292 | 100.0000 |



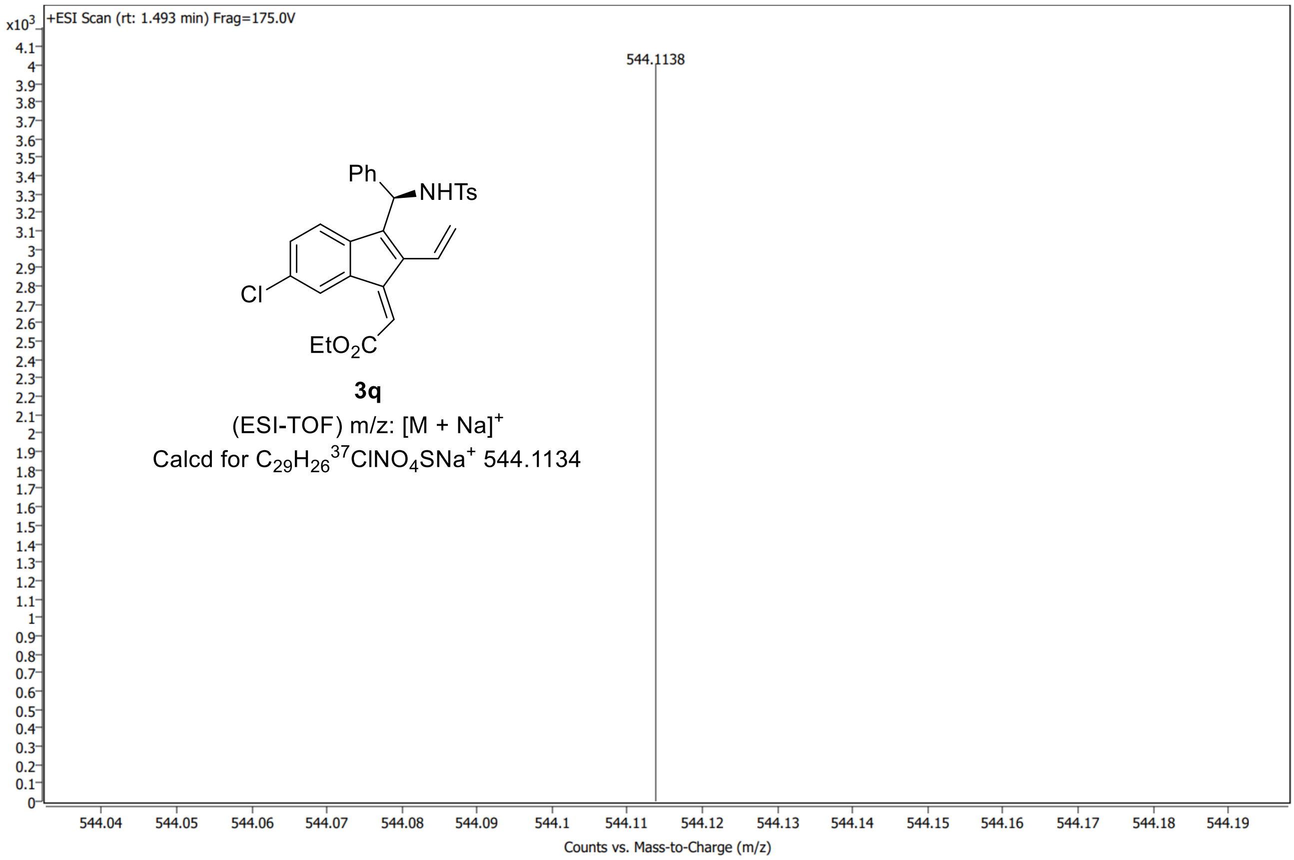
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.483 | BBA | 0.19 | 61.6714 | 752.2999 | 4.7230 |
| 7.246 | BBA | 0.24 | 977.9205 | 15176.1416 | 95.2770 |
| | | | Totals: | 15928.4415 | 100.0000 |



**3q**

(ESI-TOF) m/z: [M + Na]$^+$

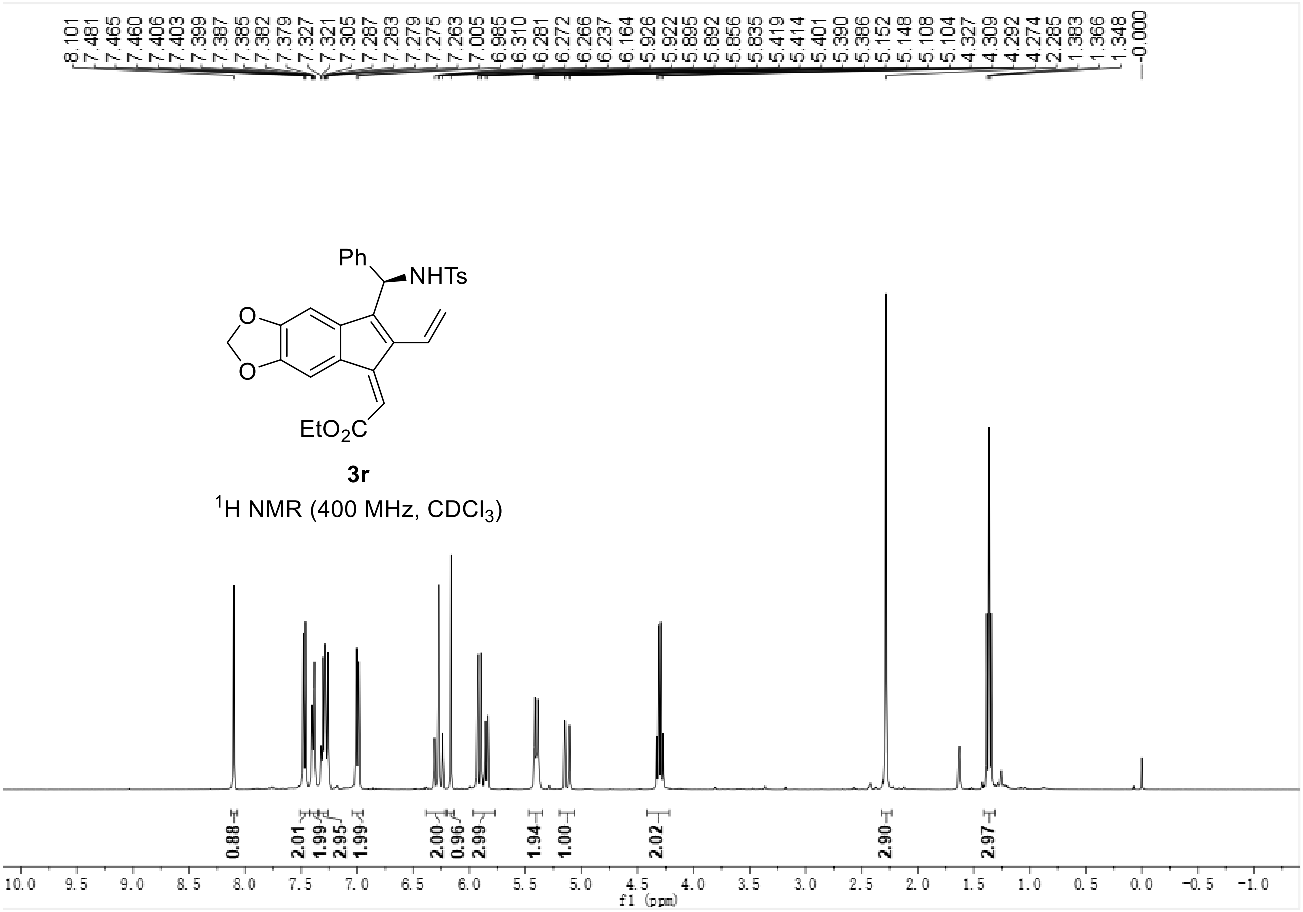
Calcd for $C_{29}H_{26}{}^{35}ClNO_4SNa^+$ 542.1163



**3q**

(ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{29}H_{26}{}^{37}ClNO_4SNa^+$ 544.1134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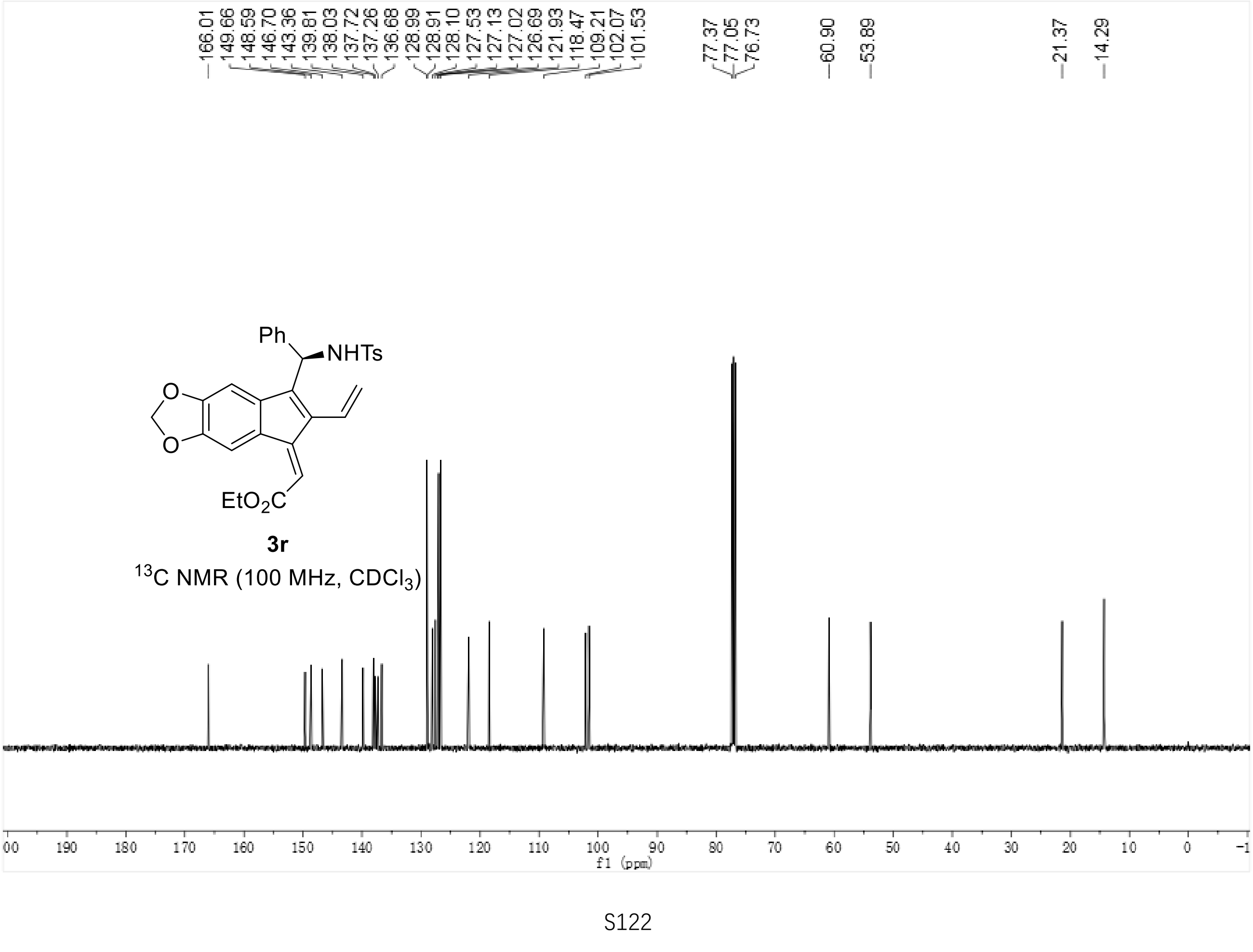
7.403
7.399
7.387
7.385
7.382
7.379
7.327
7.321
7.305
7.287
7.283
7.279
7.275
7.263
7.005
6.985
6.310
6.281
6.272
6.266
6.237
6.164
5.926
5.922
5.895
5.892
5.856
5.835
5.419
5.414
5.401
5.390
5.386
5.152
5.148
5.108
5.104
4.327
4.309
4.292
4.274
2.285
1.383
1.366
1.348
-0.000
Ph
NHTs
O
O
EtO2C
3r
1H NMR (400 MHz, CDCl3)
0.88
2.01
1.99
2.95
1.99
2.00
0.96
2.99
1.94
1.00
2.02
2.90
2.97
f1 (ppm)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137.72
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127.13
127.02
126.69
121.93
118.47
109.21
102.07
101.53
77.37
77.05
76.73
60.90
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14.29
Ph
NHTs
O
O
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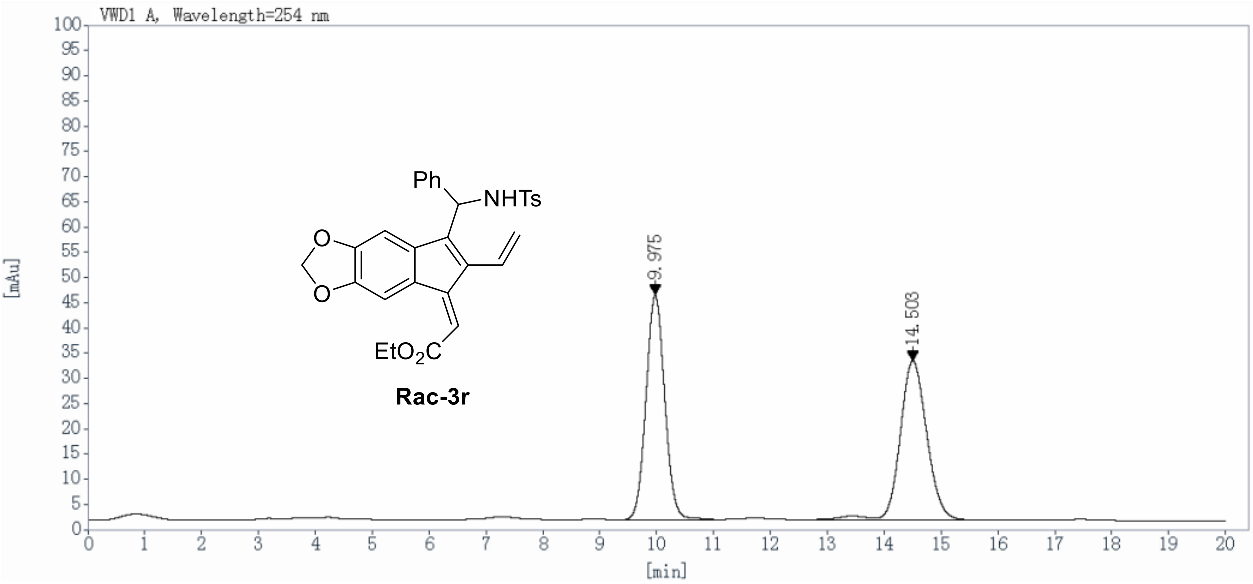
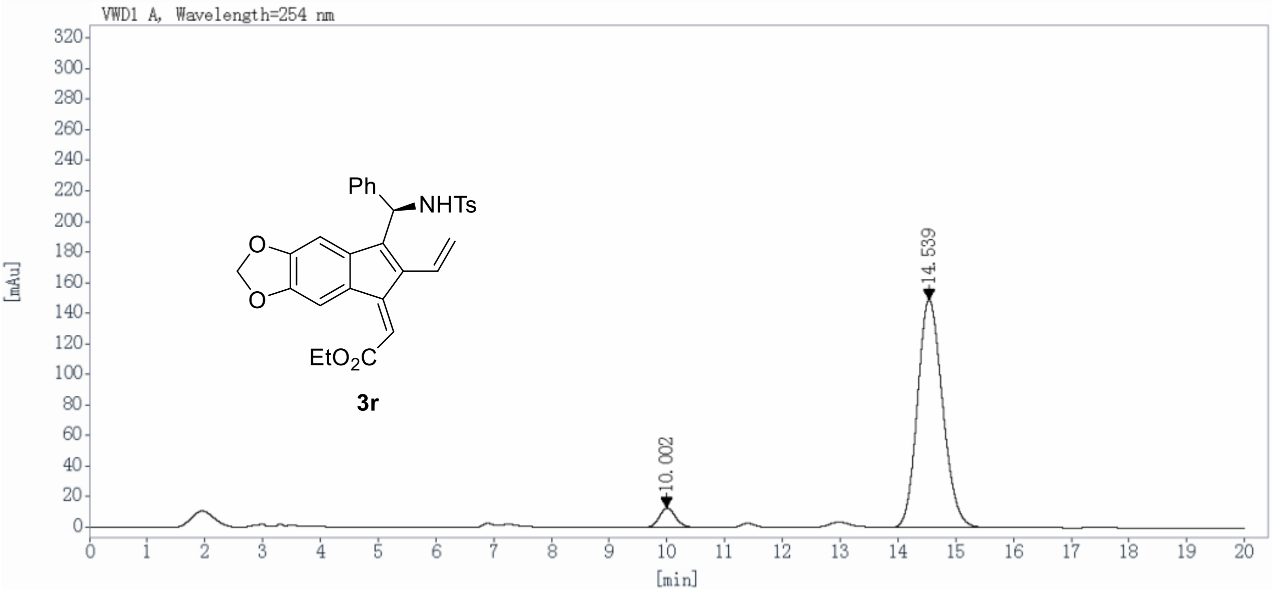
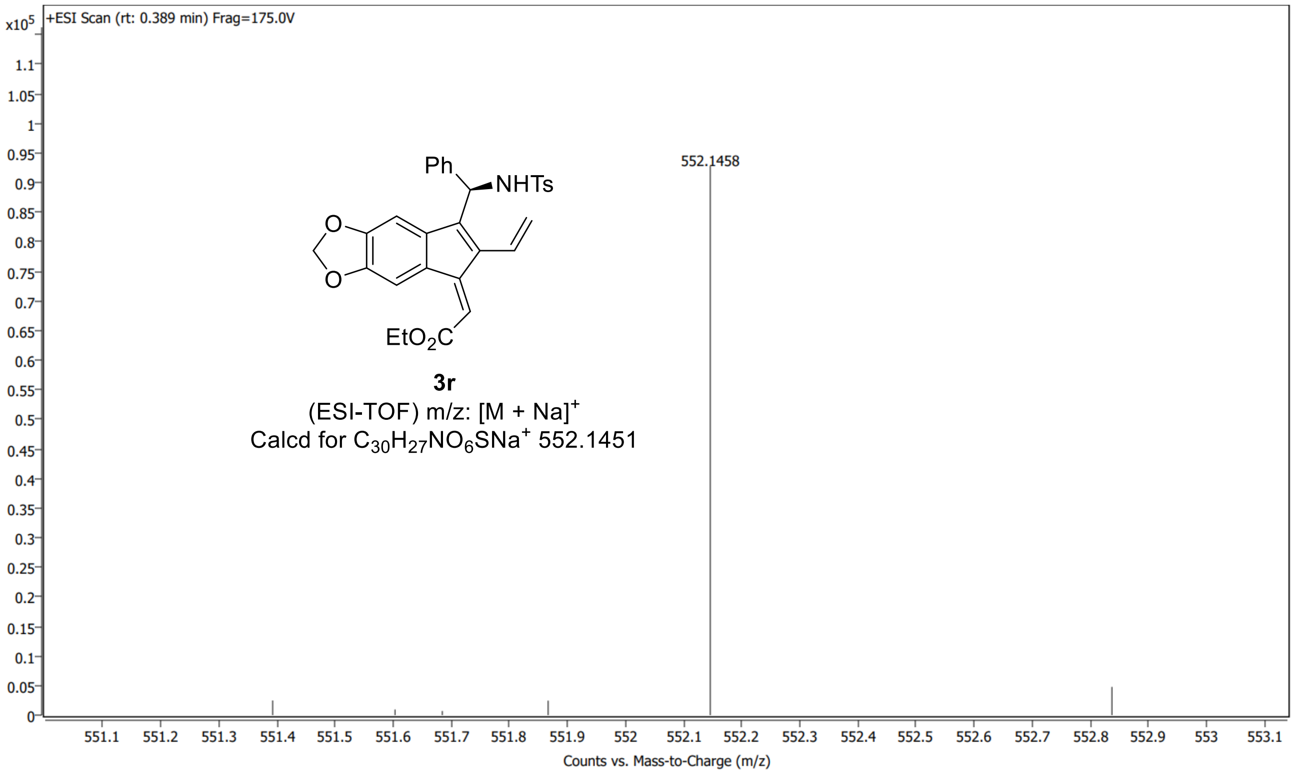
3r
13C NMR (100 MHz, CDCl3)
f1 (ppm)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.975 | BB | 0.36 | 163.2014 | 3737.9814 | 49.4434 |
| 14.503 | VB R | 0.50 | 115.6183 | 3822.1433 | 50.5566 |
| | | | Totals: | 7560.1248 | 100.0000 |



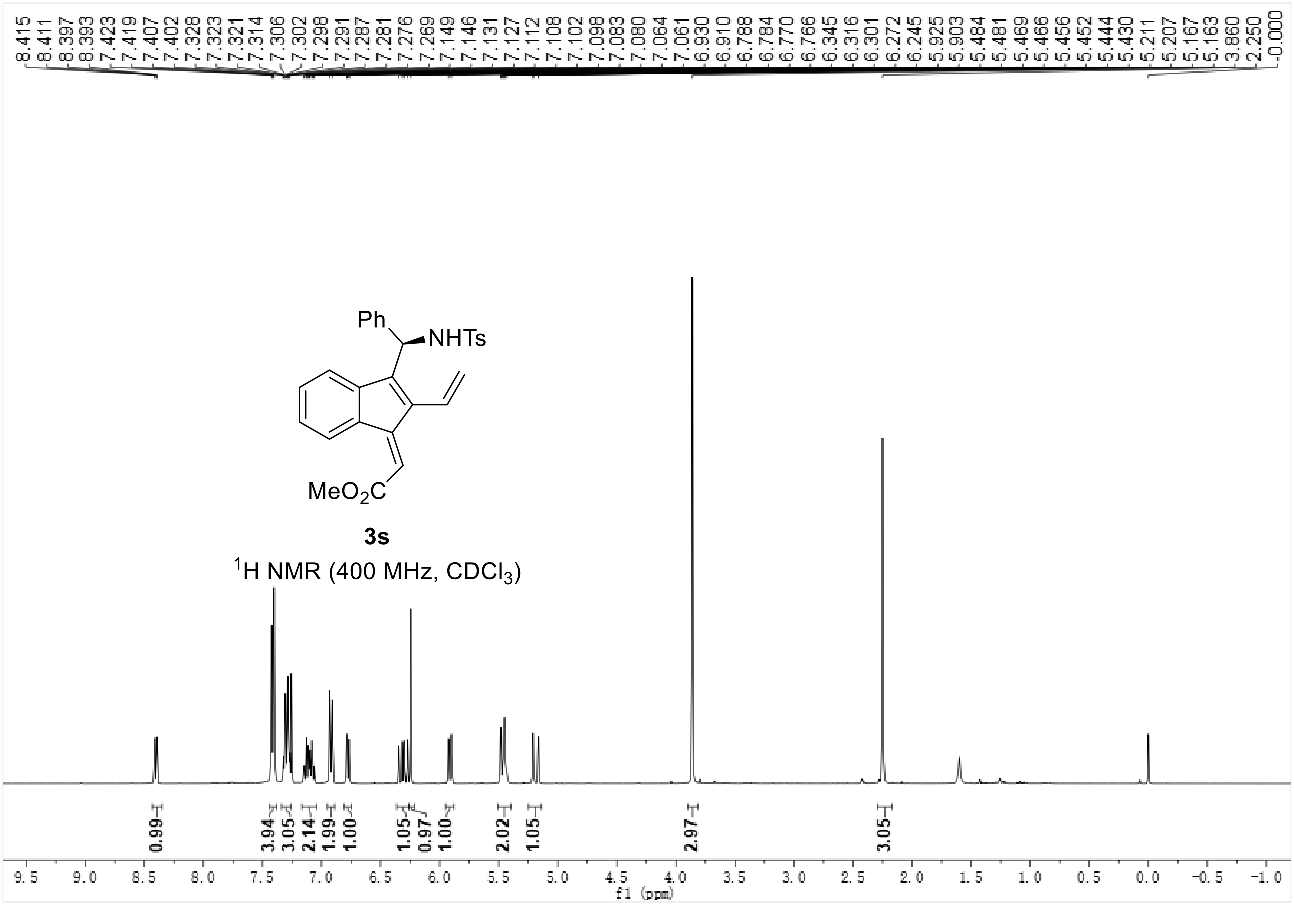
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 10.002 | BB | 0.29 | 12.6019 | 238.6169 | 5.0184 |
| 14.539 | BB | 0.47 | 149.6136 | 4516.2368 | 94.9816 |
| | | | Totals: | 4754.8537 | 100.0000 |



**3r**

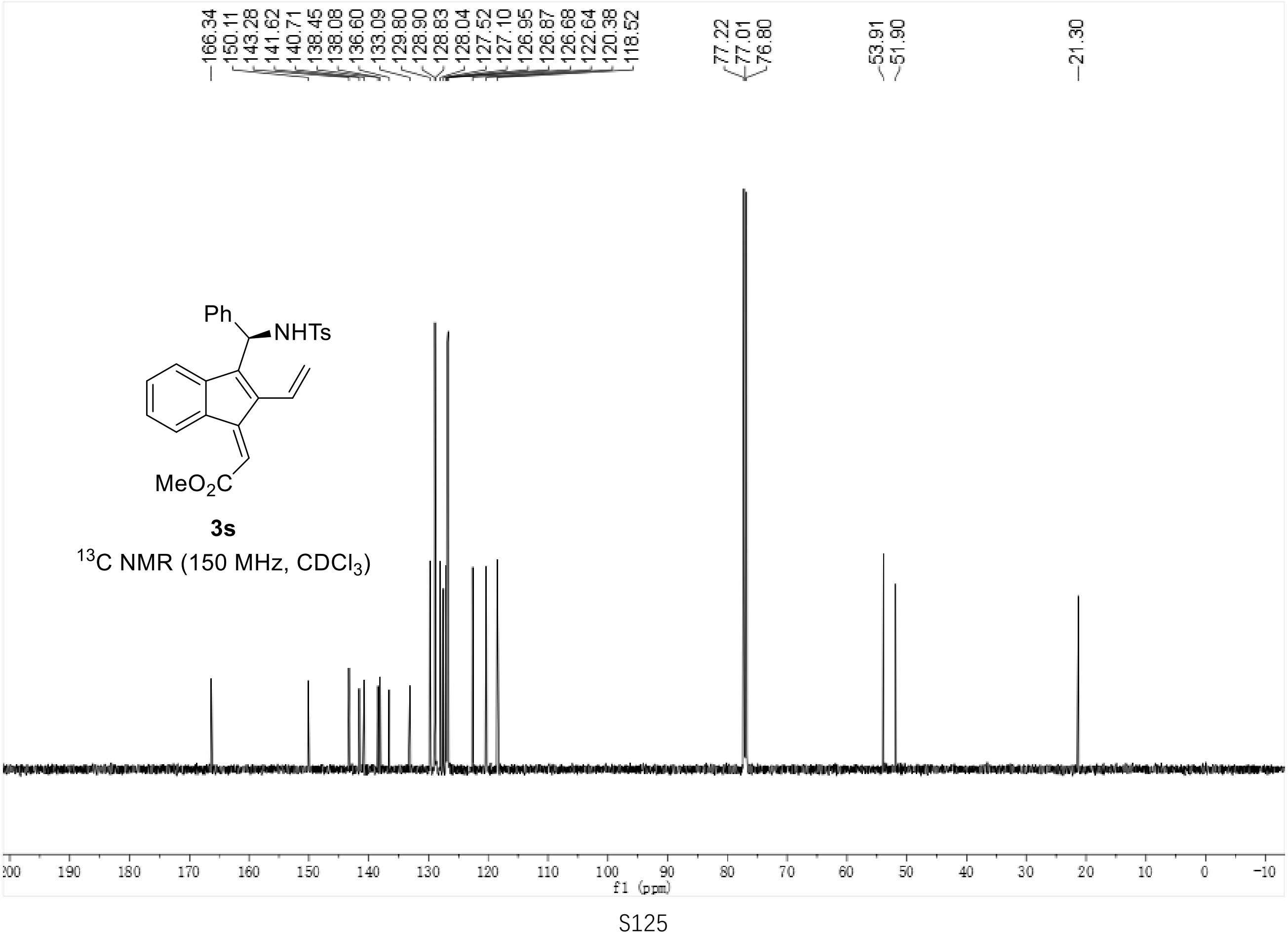
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{27}NO_6SNa^+$ 552.1451



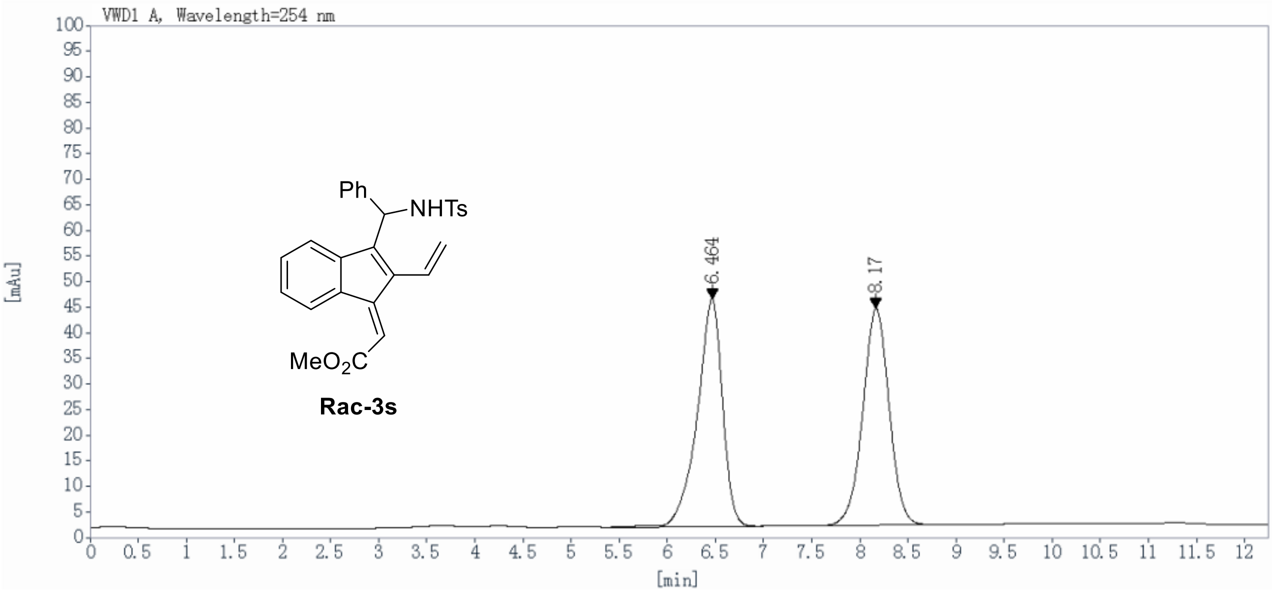
**3s**

$^1$H NMR (400 MHz, $CDCl_3$)

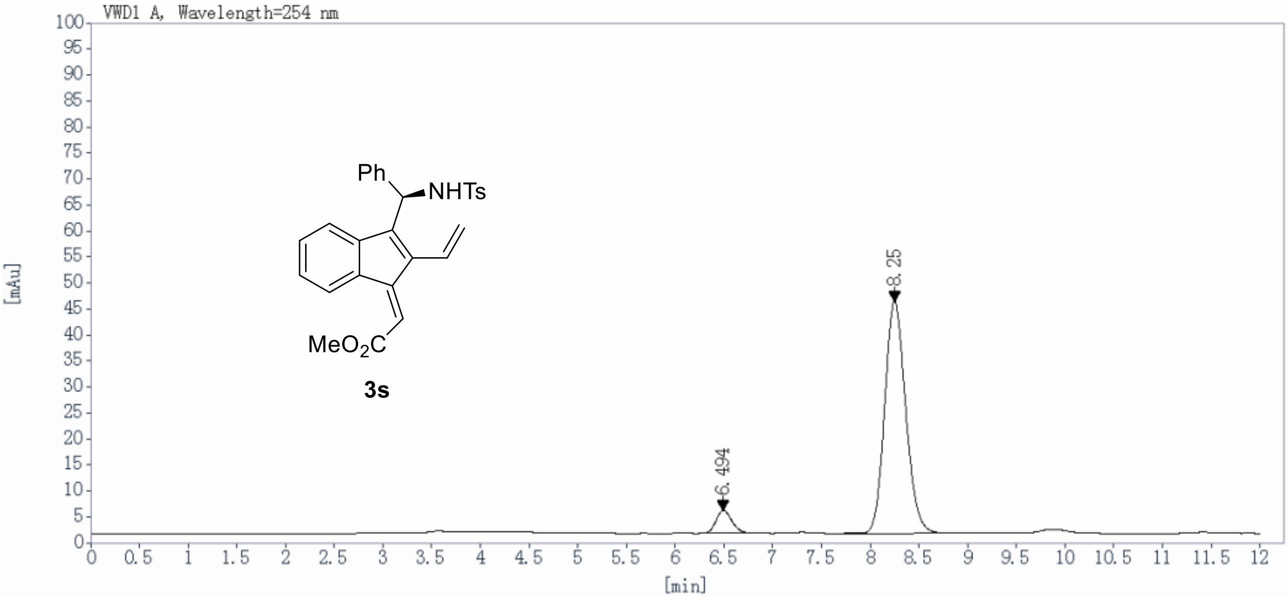


**3s**

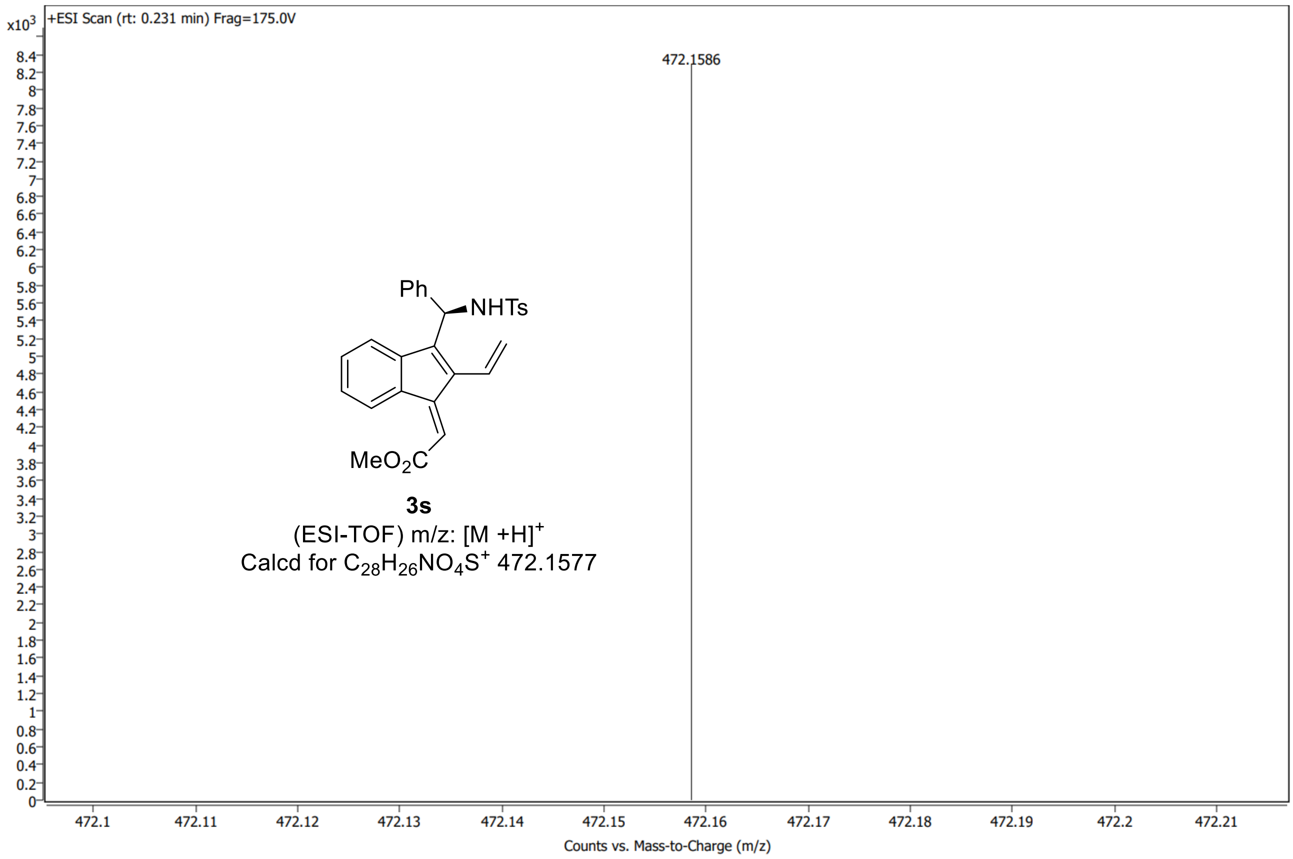
$^{13}$C NMR (150 MHz, $CDCl_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.464 | VV R | 0.27 | 442.7633 | 8097.3701 | 50.1978 |
| 8.170 | BB | 0.29 | 421.5631 | 8033.5498 | 49.8022 |
| | | | Totals: | 16130.9199 | 100.0000 |



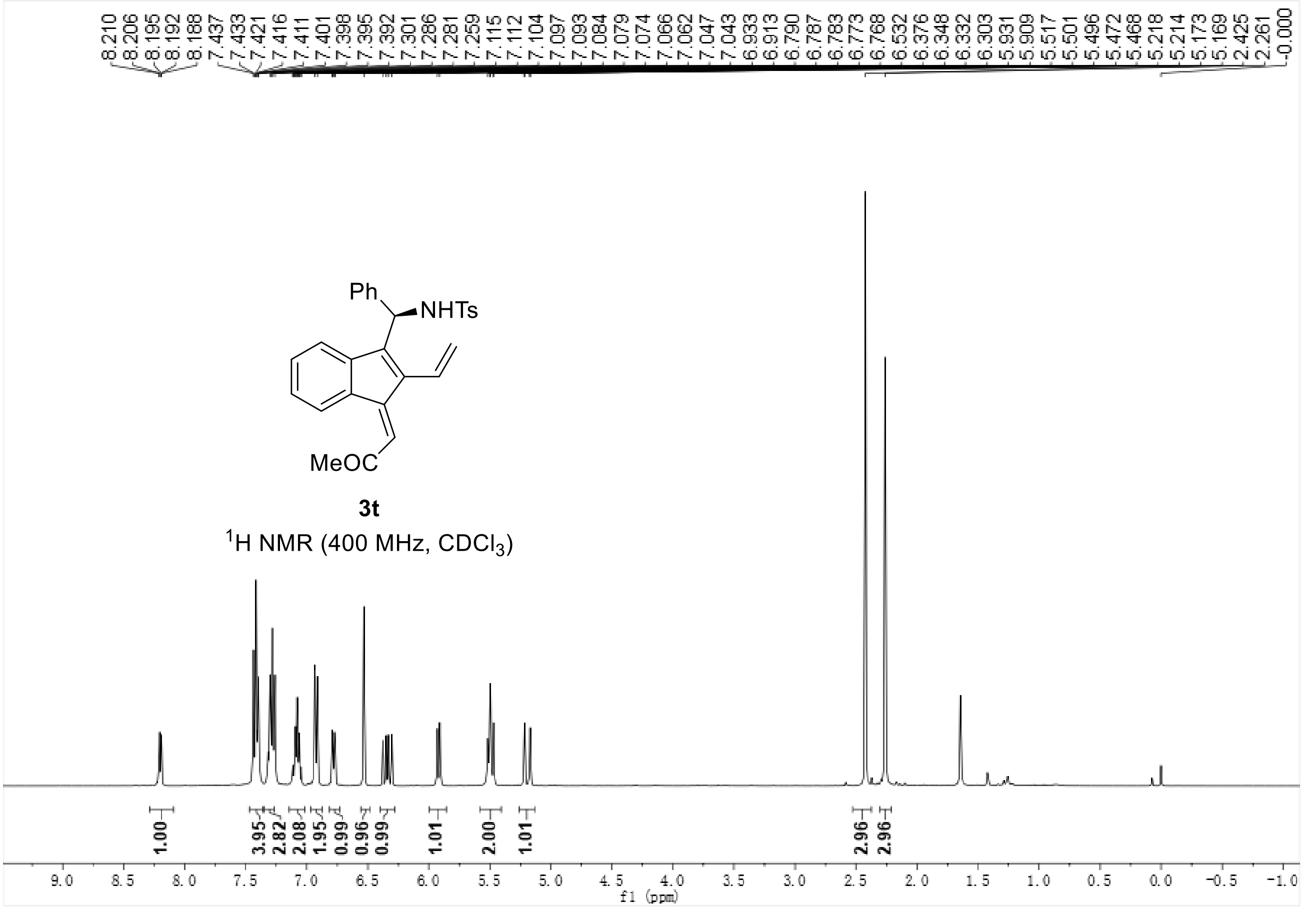
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.494 | BBA | 0.17 | 89.4755 | 988.5721 | 6.6971 |
| 8.250 | BB | 0.23 | 916.9753 | 13772.6953 | 93.3029 |
| | | | Totals: | 14761.2675 | 100.0000 |



**3s**

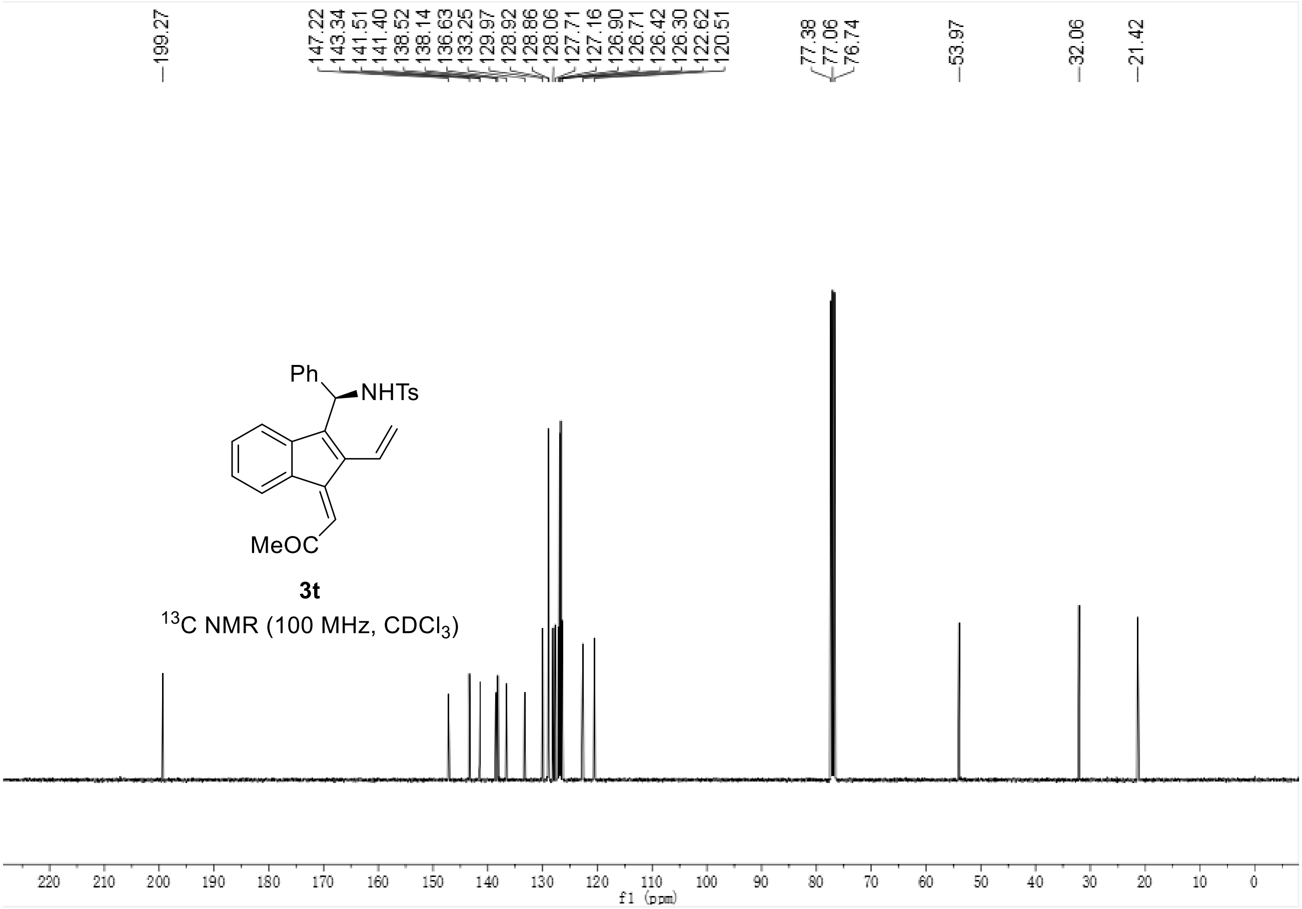
(ESI-TOF) m/z: $[M + H]^+$

Calcd for $C_{28}H_{26}NO_4S^+$ 472.1577



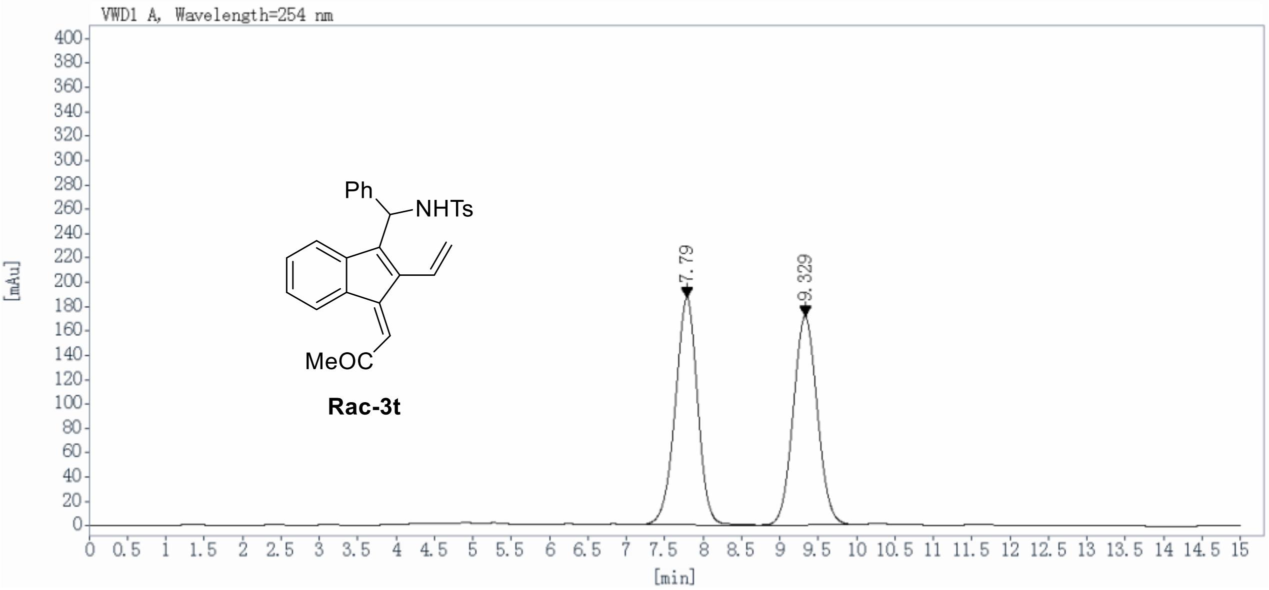
**3t**

$^{1}$H NMR (400 MHz, CDCl$_3$)

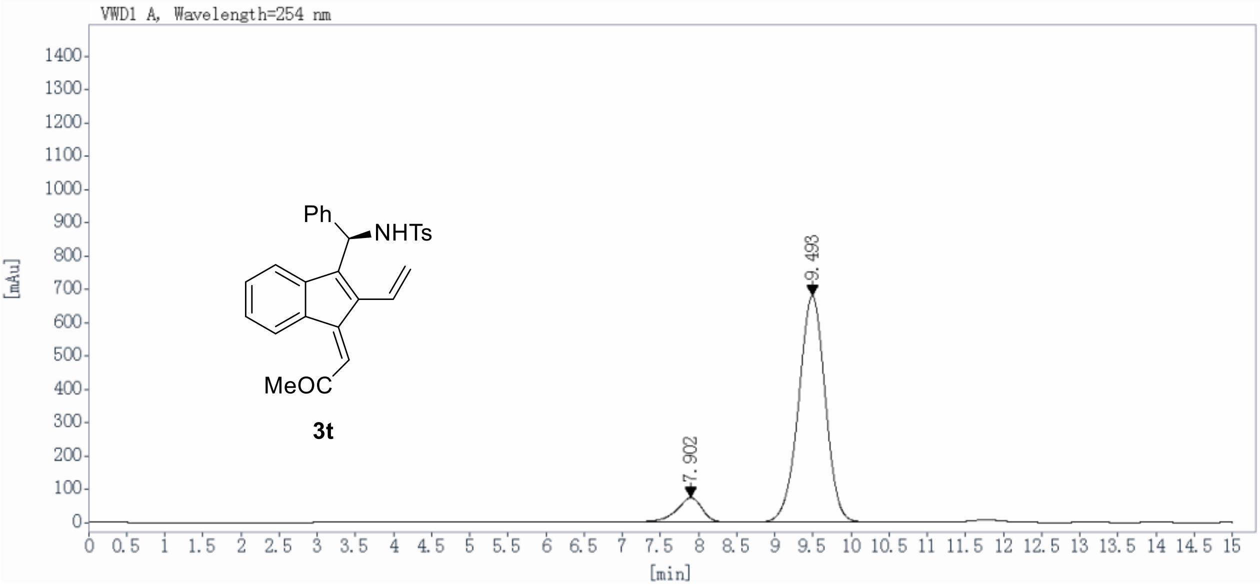


**3t**

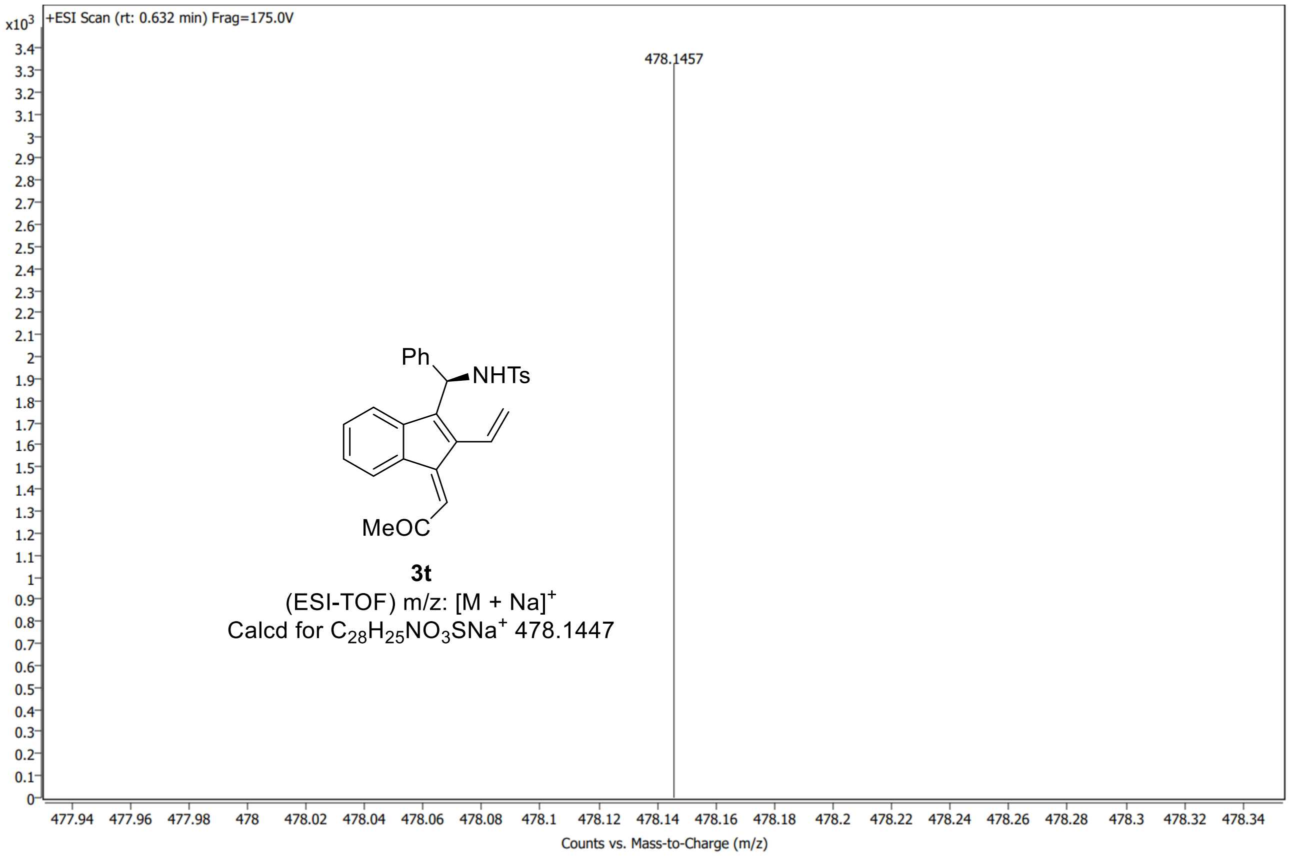
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.790 | BB | 0.31 | 186.6261 | 3789.8940 | 50.3415 |
| 9.329 | BB | 0.34 | 171.4154 | 3738.4810 | 49.6585 |
| | | | Totals: | 7528.3750 | 100.0000 |



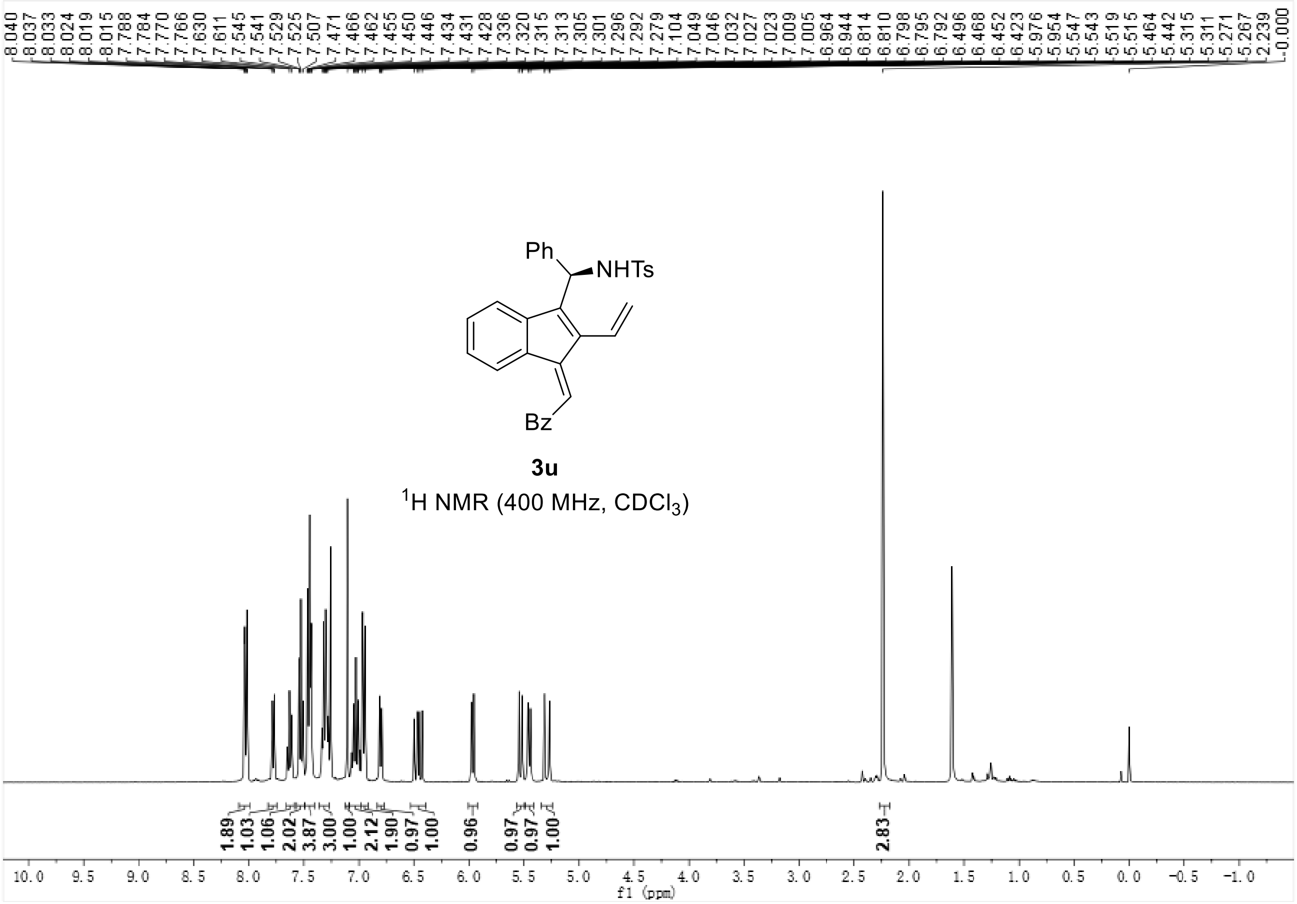
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.902 | BB | 0.35 | 73.0211 | 1679.1783 | 9.2474 |
| 9.493 | BV R | 0.37 | 679.5447 | 16479.2363 | 90.7526 |
| | | | Totals: | 18158.4147 | 100.0000 |



**3t**

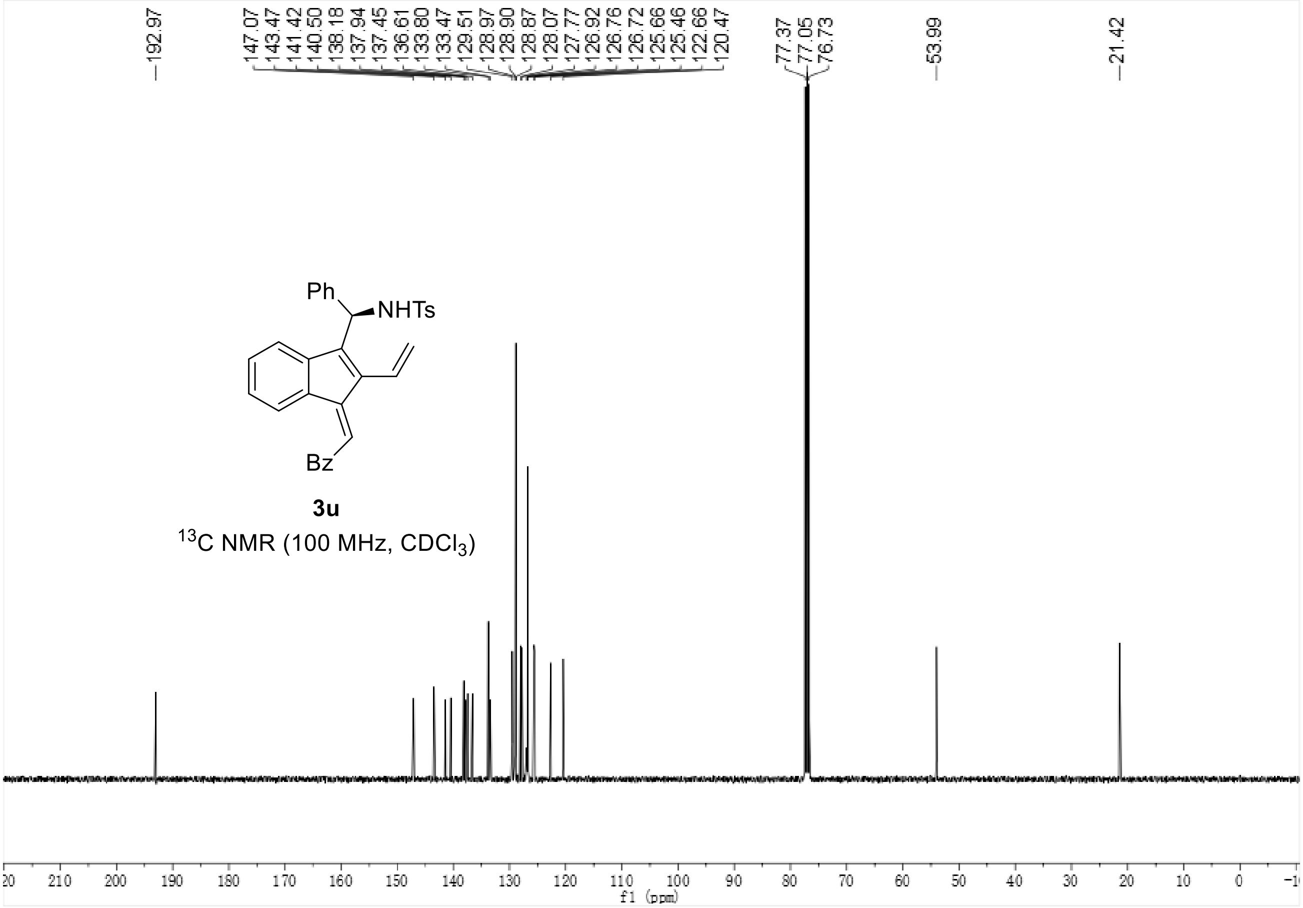
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{28}H_{25}NO_3SNa^+$ 478.1447



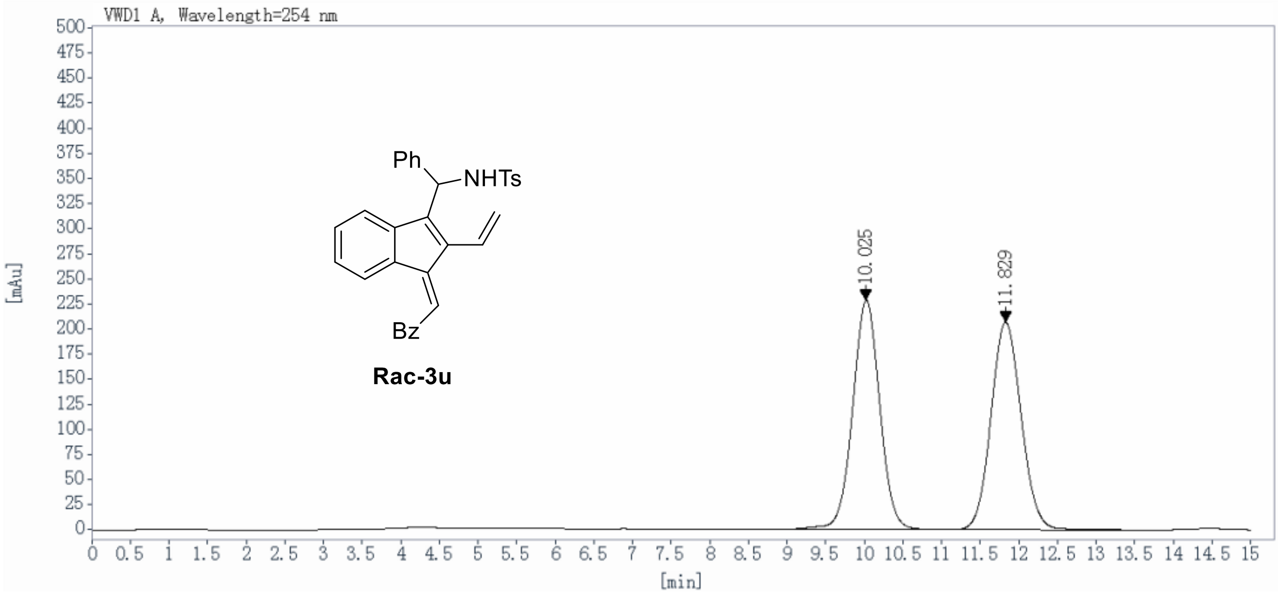
**3u**

$^1$H NMR (400 MHz, CDCl$_3$)



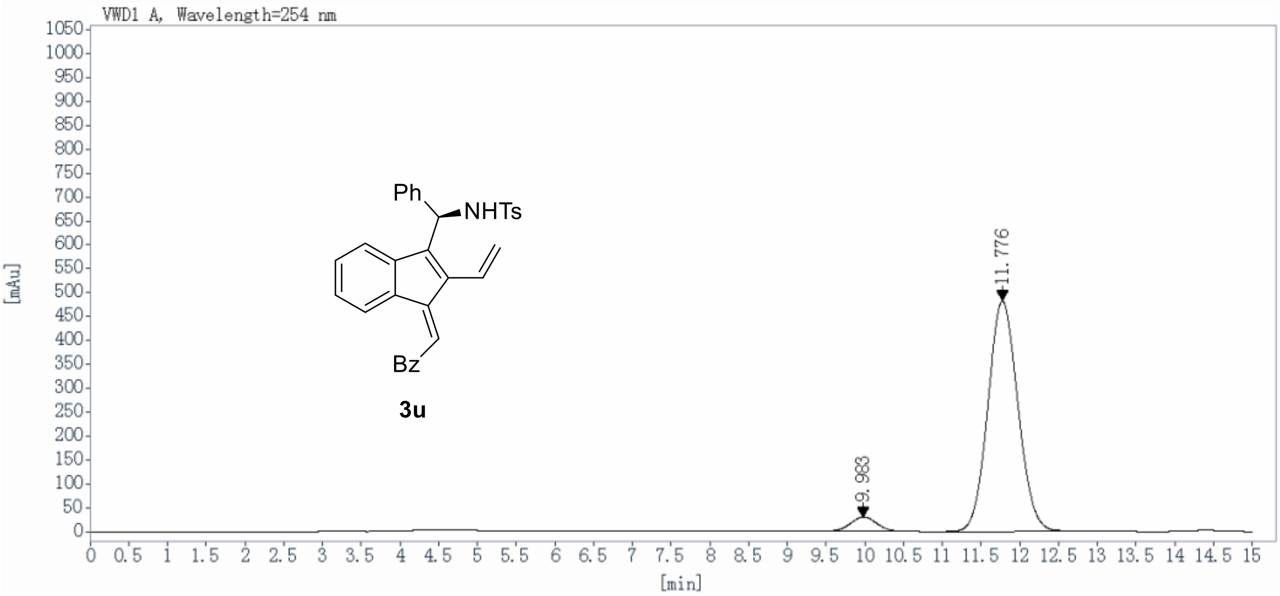
**3u**

$^{13}$C NMR (100 MHz, CDCl$_3$)



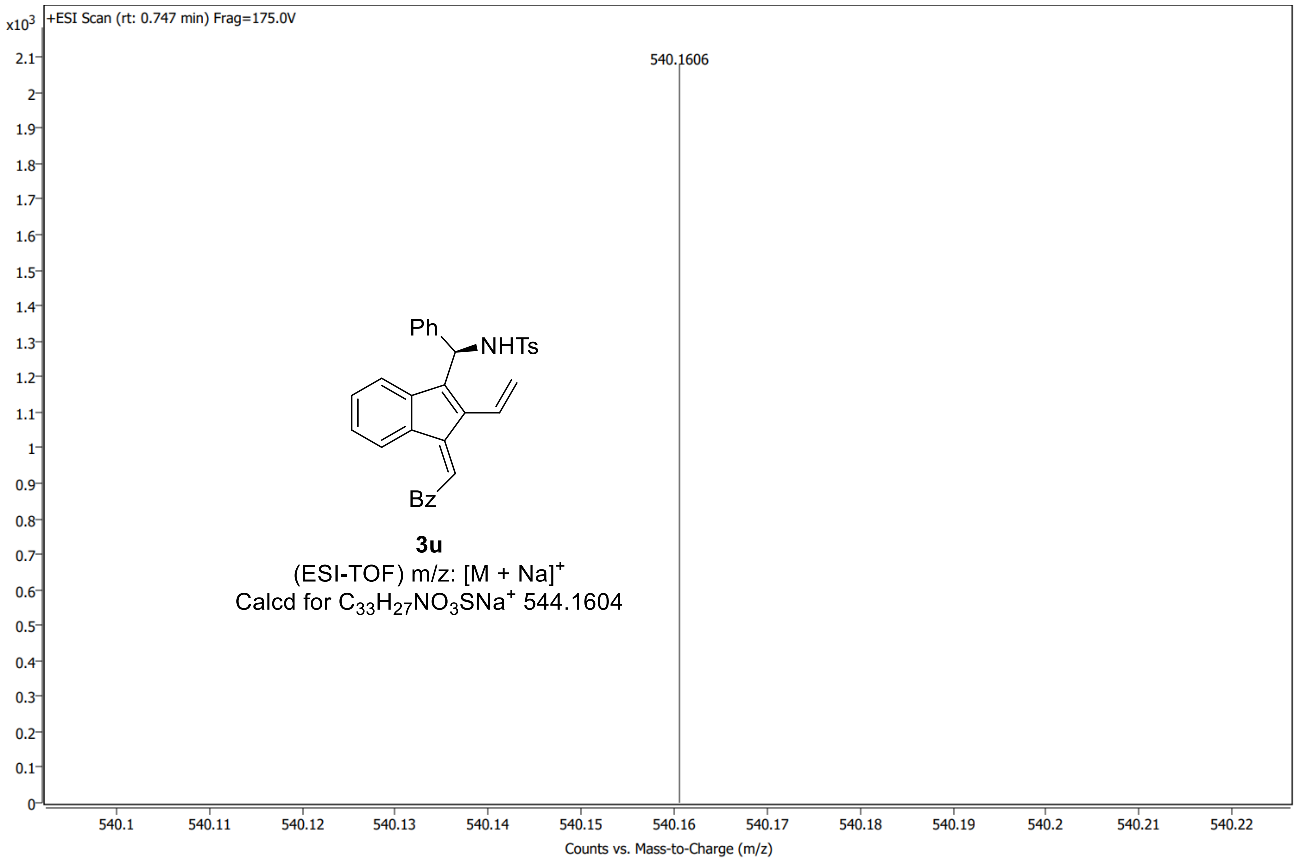
**Rac-3u**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 10.025 | BB | 0.38 | 228.3190 | 5604.2920 | 49.9059 |
| 11.829 | BB | 0.42 | 206.8966 | 5625.4287 | 50.0941 |
|  |  |  | Totals: | 11229.7207 | 100.0000 |



**3u**

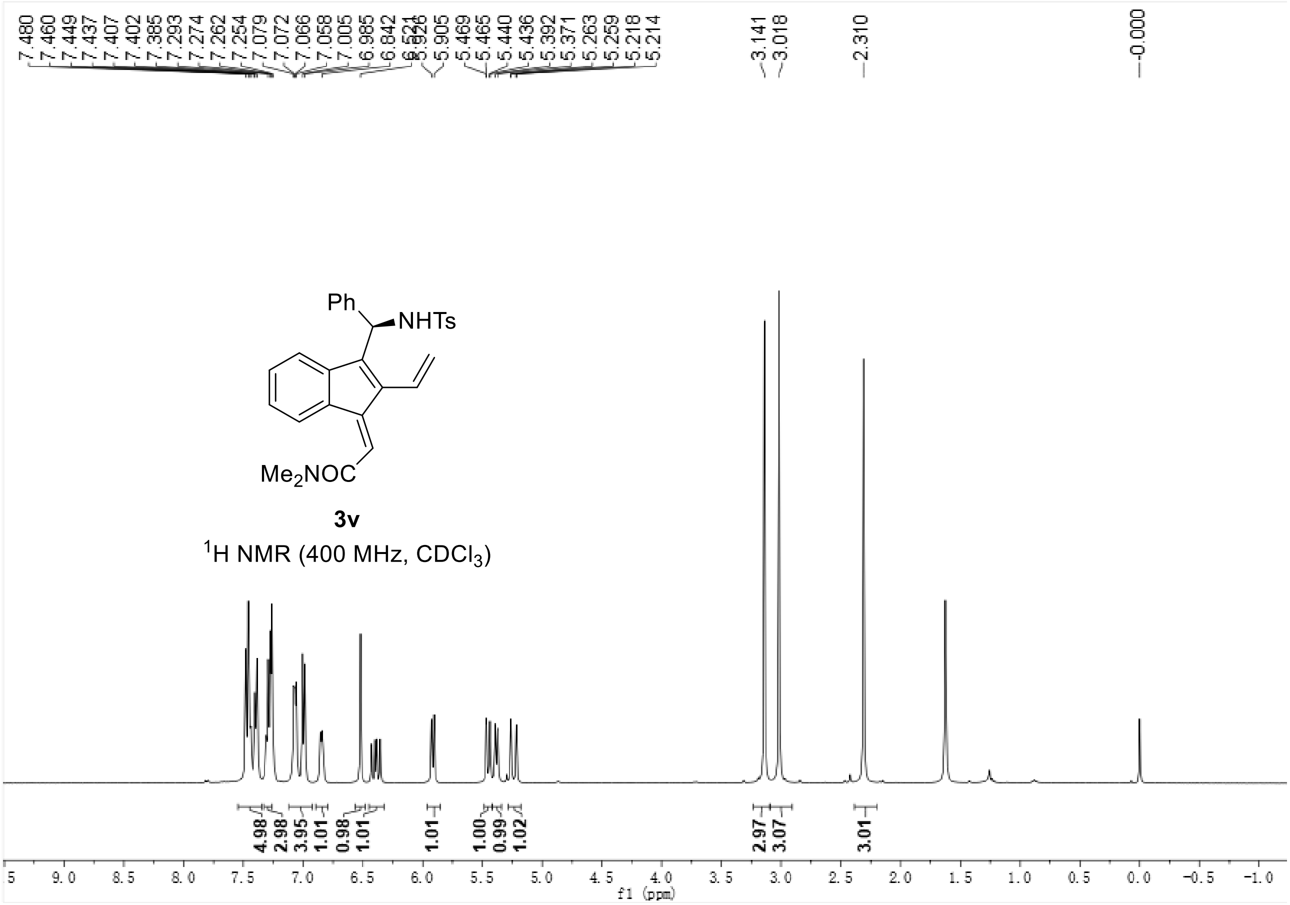
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.983 | BBA | 0.37 | 29.8991 | 716.8499 | 5.2254 |
| 11.776 | BBA | 0.42 | 481.5903 | 13001.7910 | 94.7746 |
|  |  |  | Totals: | 13718.6409 | 100.0000 |



**3u**

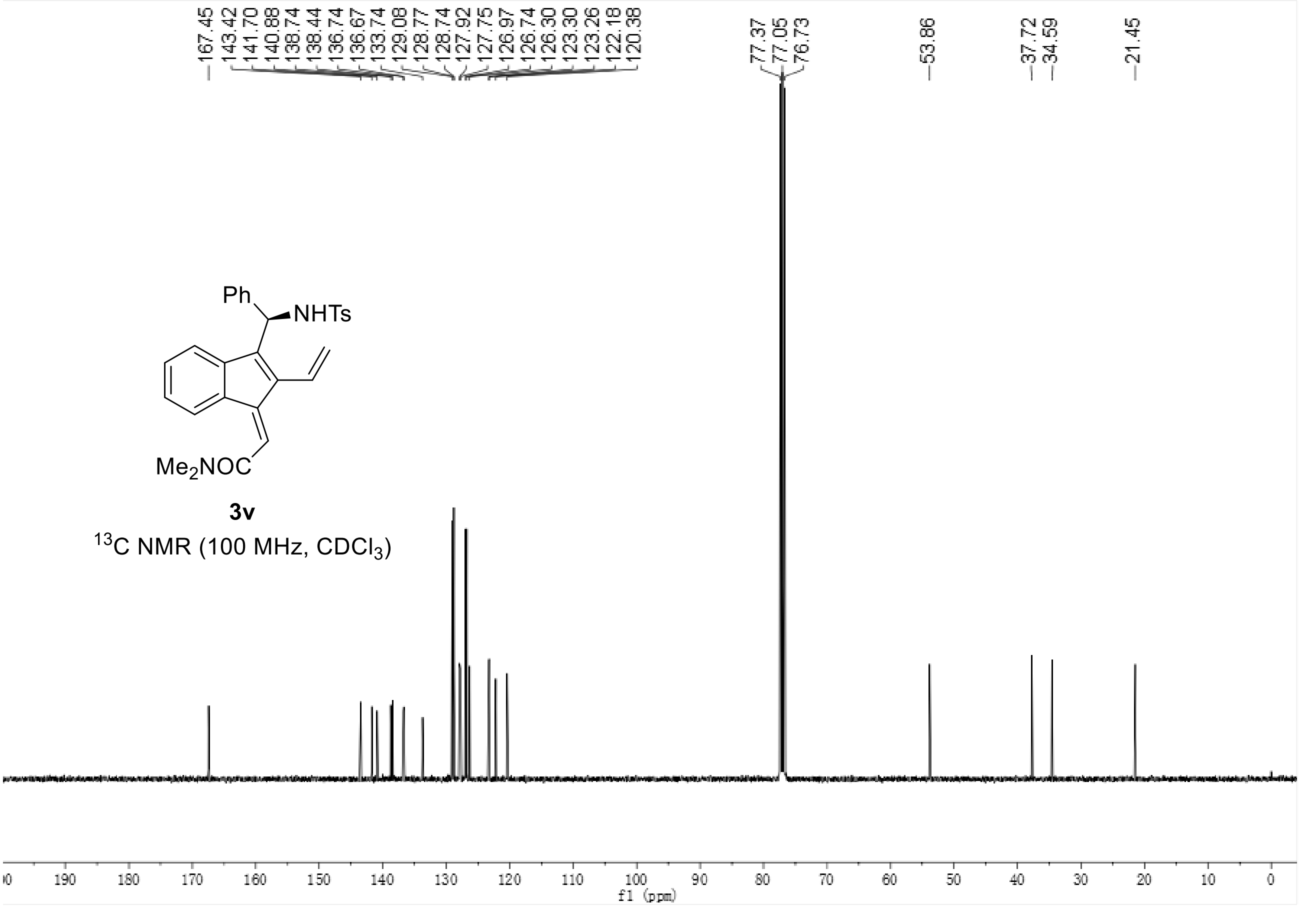
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{33}H_{27}NO_3SNa^+$ 544.1604



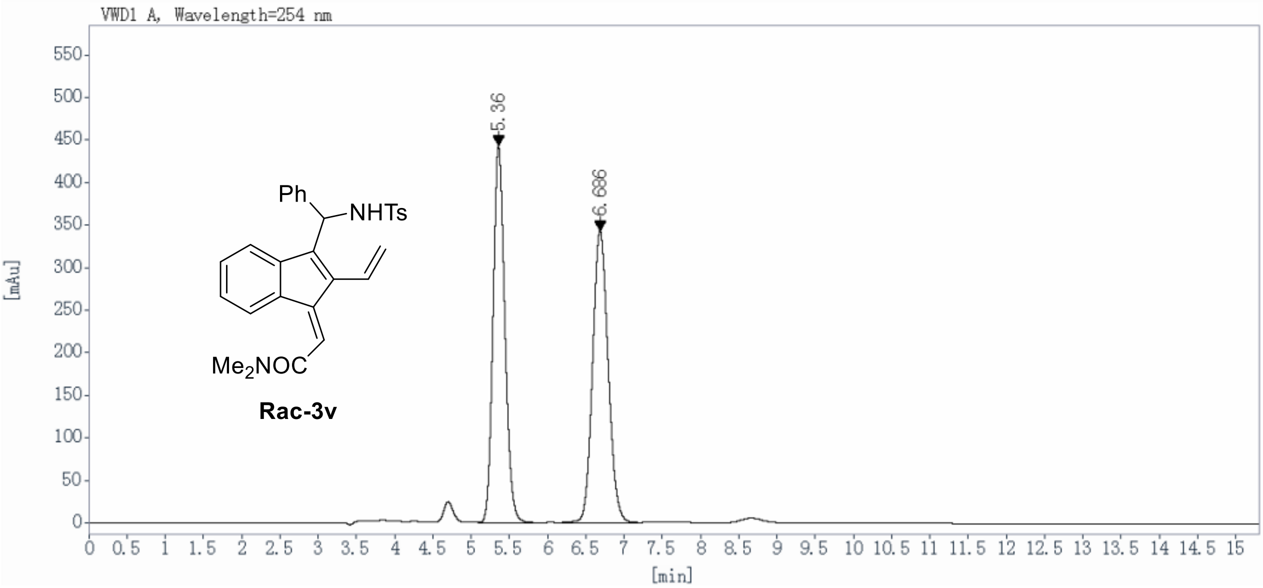
**3v**

$^1$H NMR (400 MHz, CDCl$_3$)

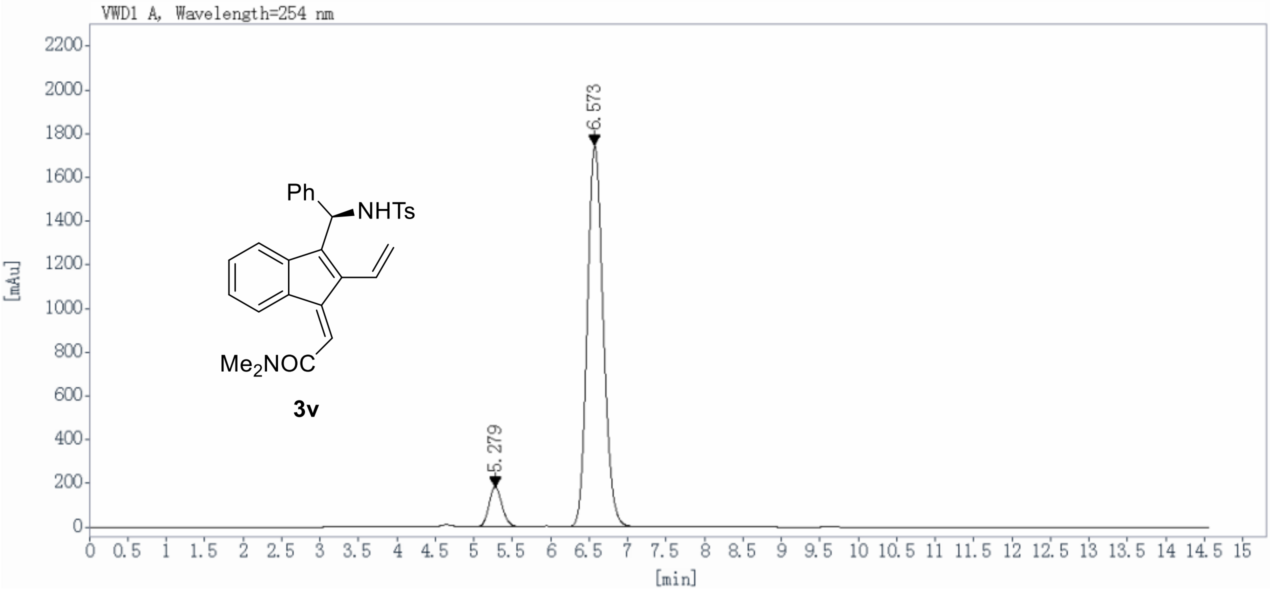


**3v**

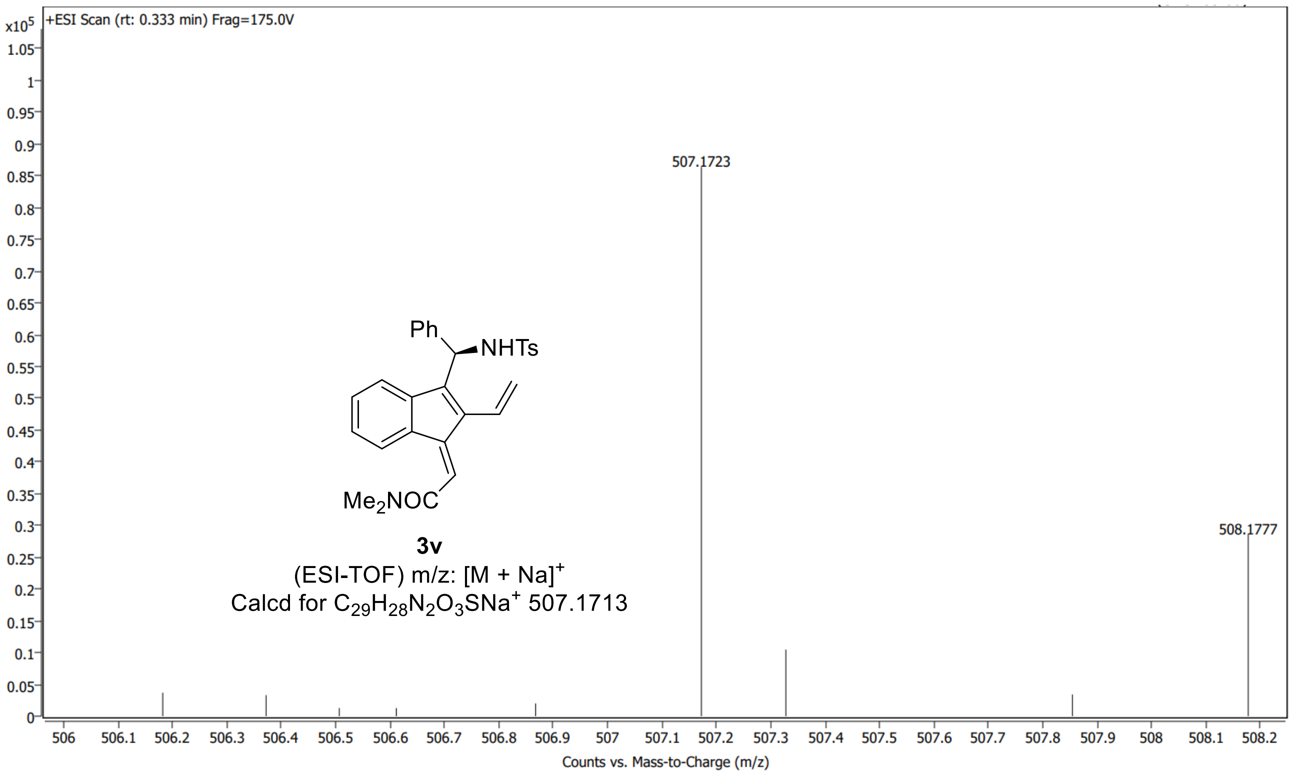
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.360 | VB | 0.17 | 442.6902 | 4793.8110 | 49.8529 |
| 6.686 | BB | 0.22 | 342.9724 | 4822.0962 | 50.1471 |
| | | | Totals: | 9615.9072 | 100.0000 |



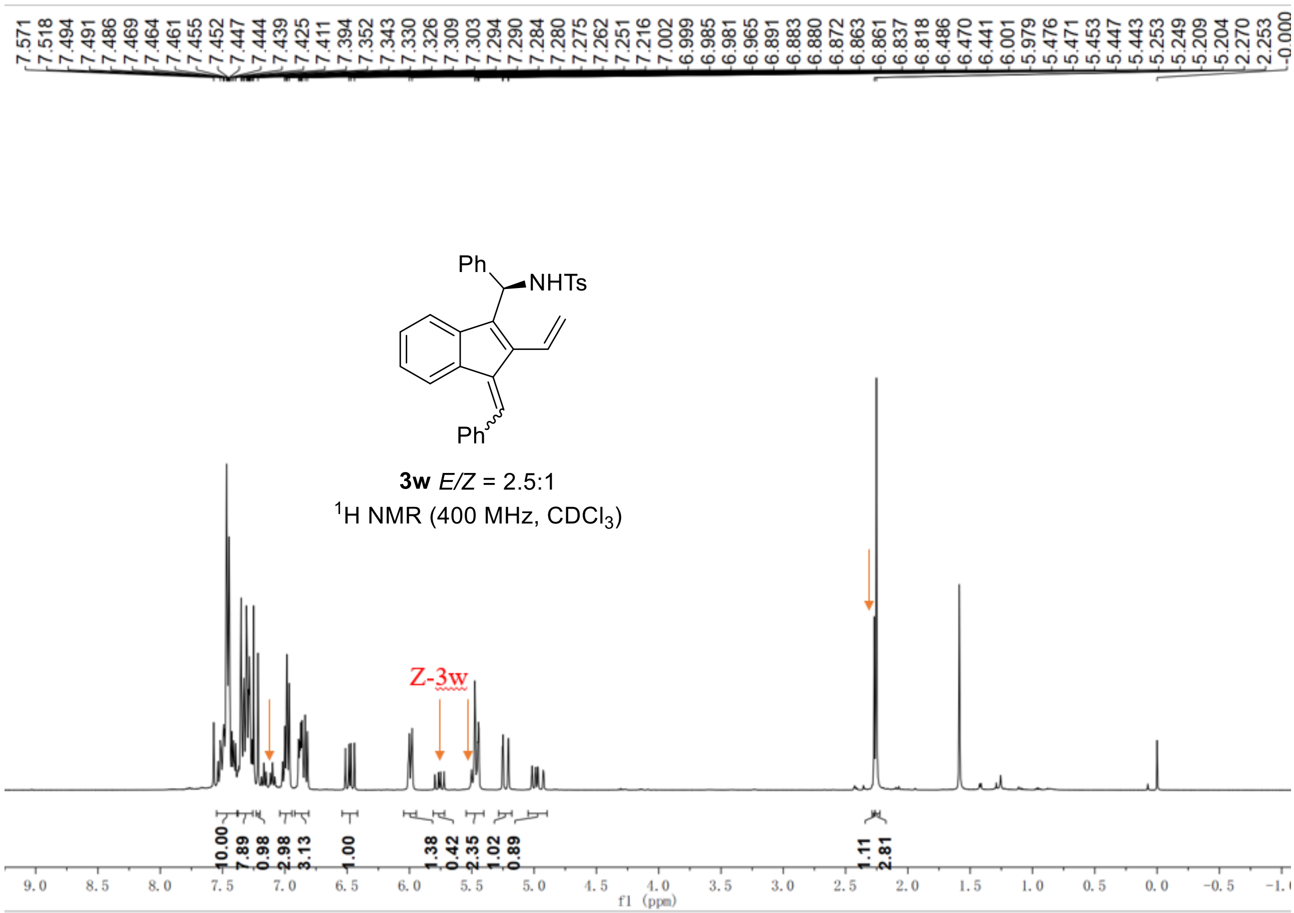
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.279 | BBA | 0.18 | 181.3925 | 2094.7332 | 7.6337 |
| 6.573 | BB | 0.23 | 1744.3359 | 25345.7695 | 92.3663 |
| | | | Totals: | 27440.5027 | 100.0000 |



**3v**

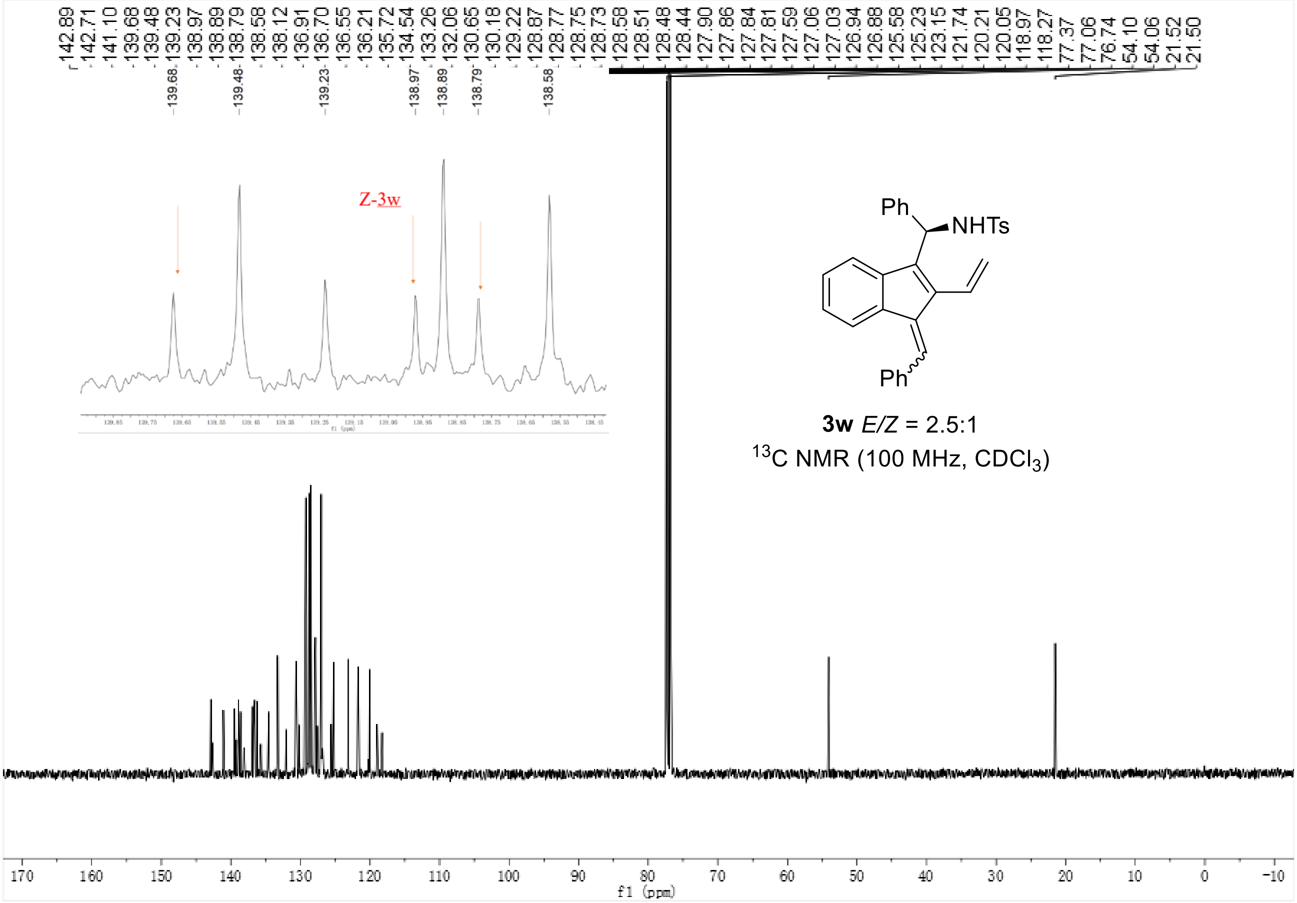
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{29}H_{28}N_2O_3SNa^+$ 507.1713



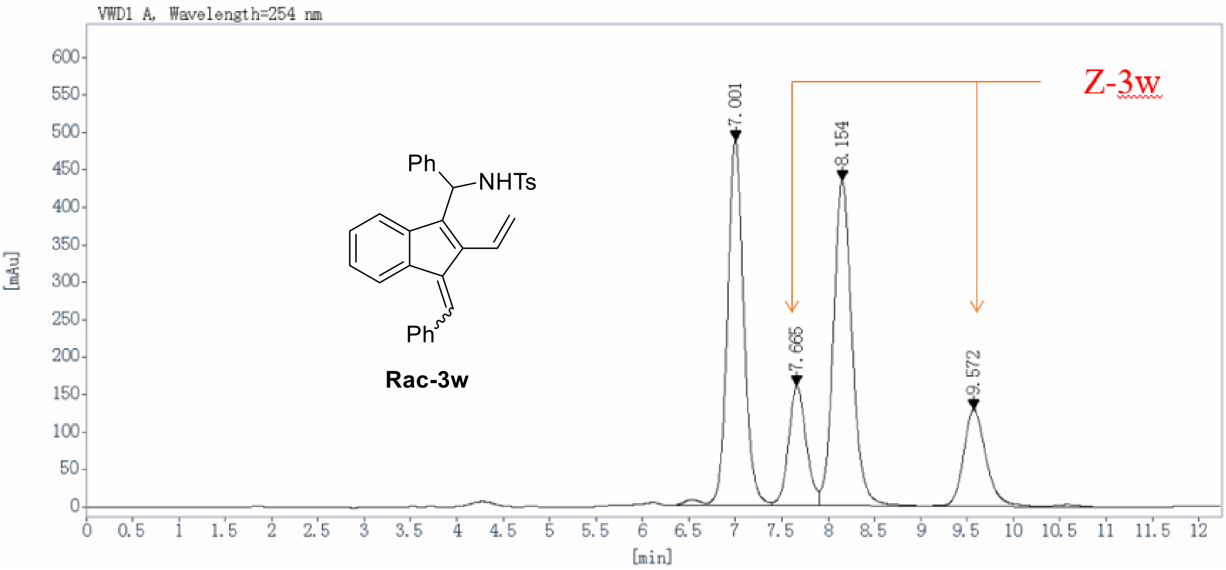
**3w** *E*/*Z* = 2.5:1

$^1$H NMR (400 MHz, CDCl$_3$)

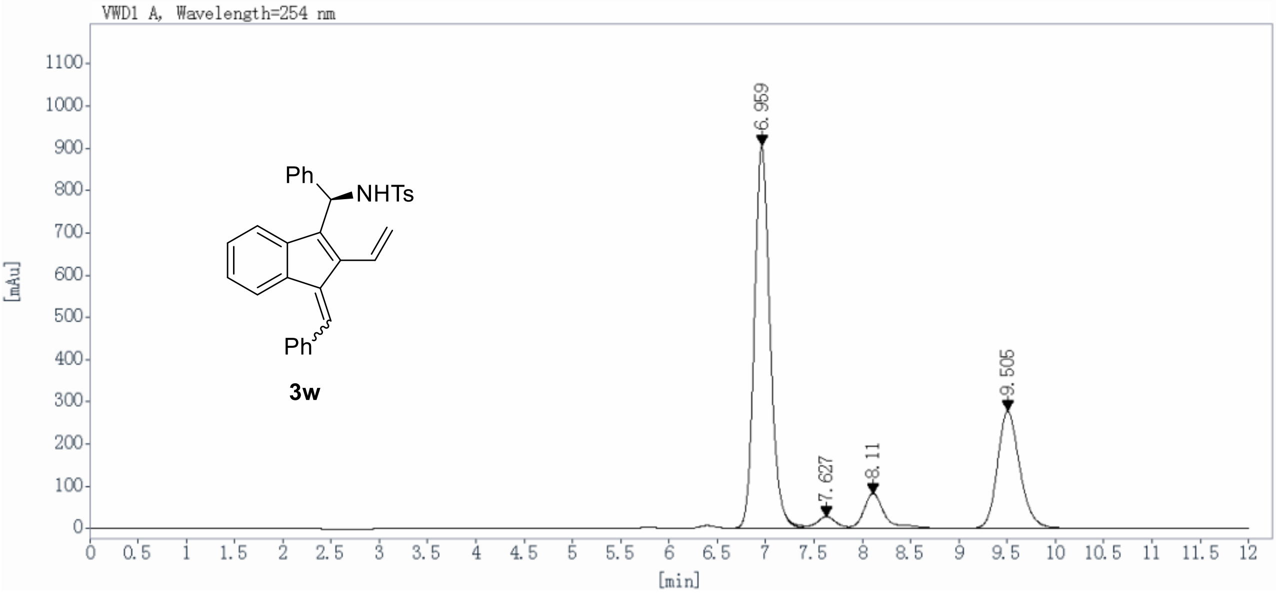


**3w** *E*/*Z* = 2.5:1

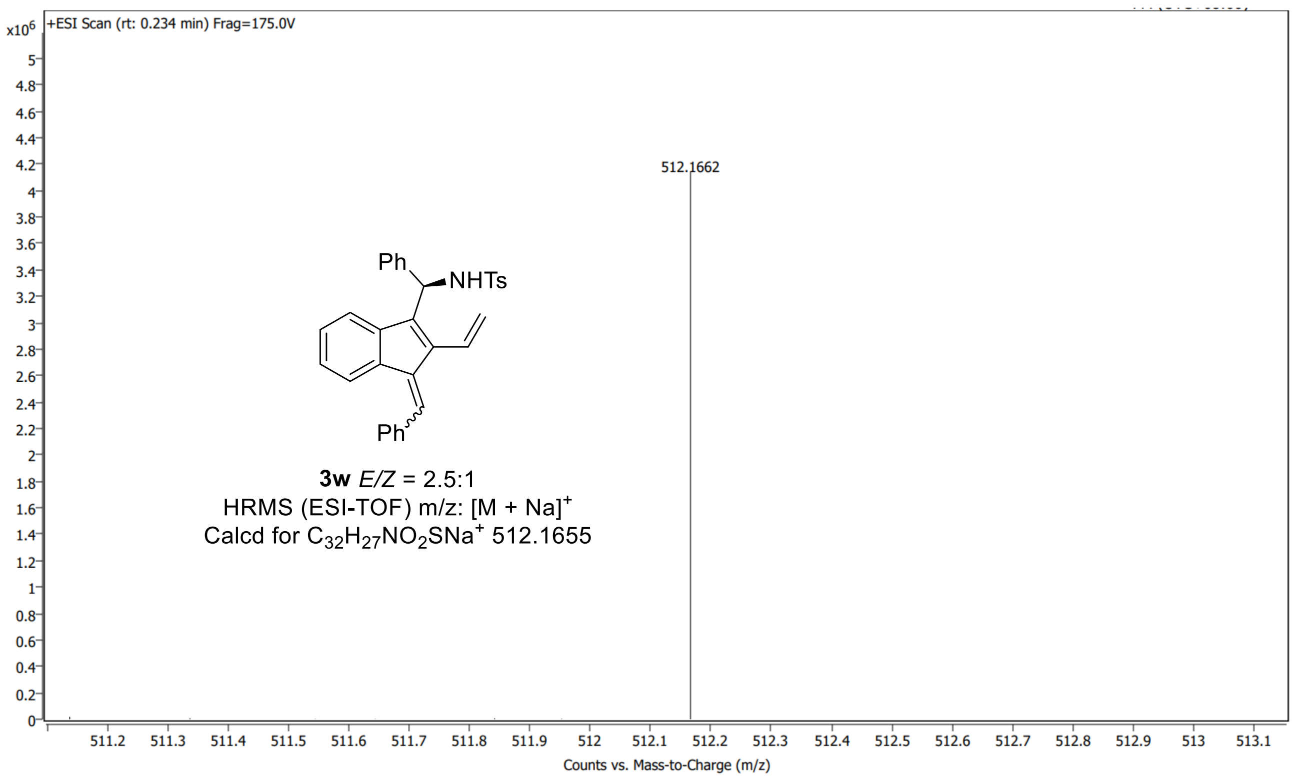
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.001 | VV R | 0.19 | 487.3712 | 6050.2515 | 36.7616 |
| 7.665 | VV | 0.20 | 159.5610 | 2123.4250 | 12.9020 |
| 8.154 | VB | 0.21 | 434.0111 | 6069.0122 | 36.8756 |
| 9.572 | BV R | 0.26 | 129.0926 | 2215.3716 | 13.4607 |
|  |  |  | Totals: | 16458.0603 | 100.0000 |



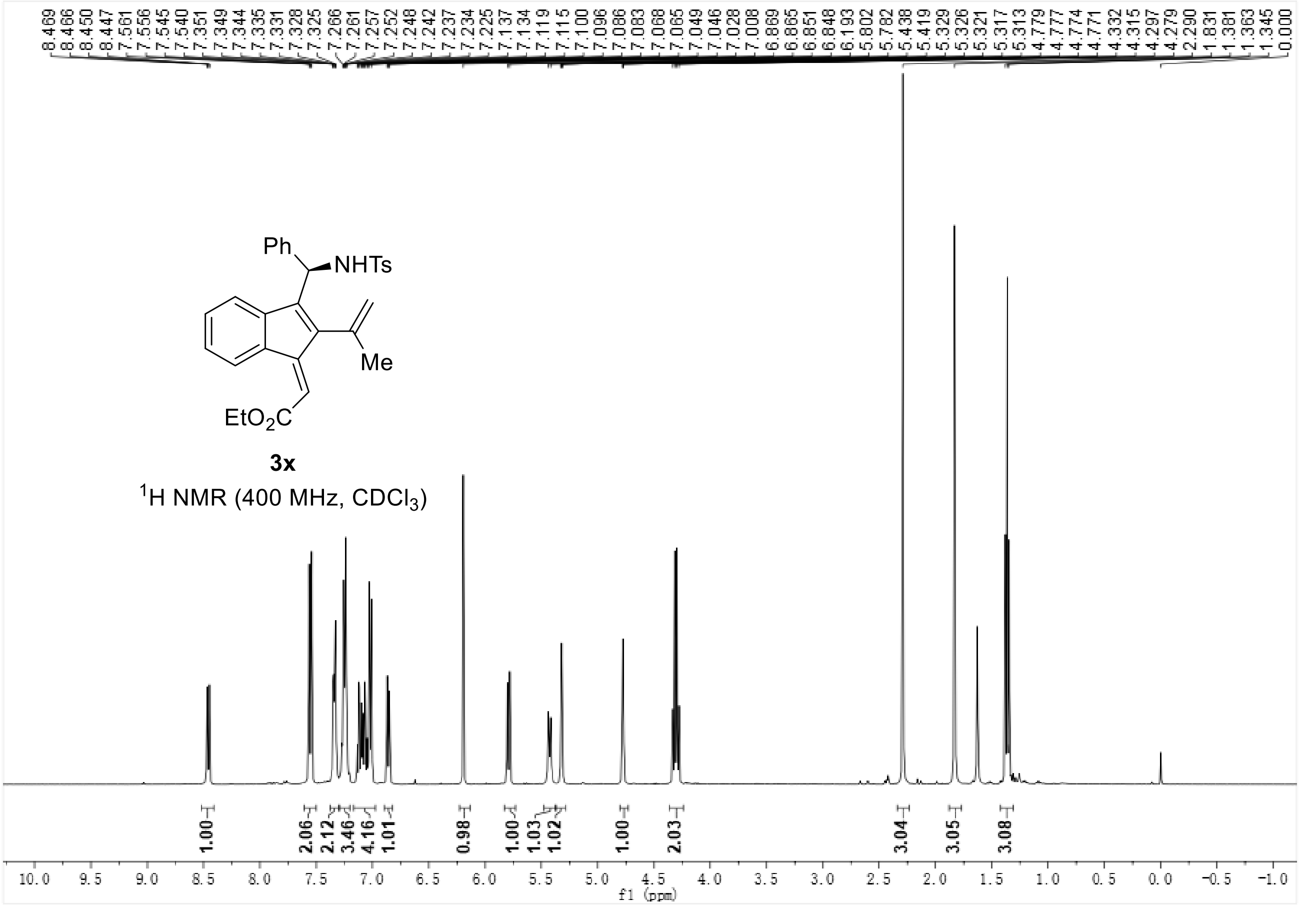
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.959 | BV R | 0.17 | 904.9175 | 10227.6650 | 62.4177 |
| 7.627 | VV E | 0.22 | 27.6450 | 416.7686 | 2.5435 |
| 8.110 | VB | 0.22 | 82.3834 | 1220.4019 | 7.4479 |
| 9.505 | BB | 0.25 | 277.7930 | 4521.0156 | 27.5910 |
|  |  |  | Totals: | 16385.8511 | 100.0000 |



**3w** *E/Z* = 2.5:1

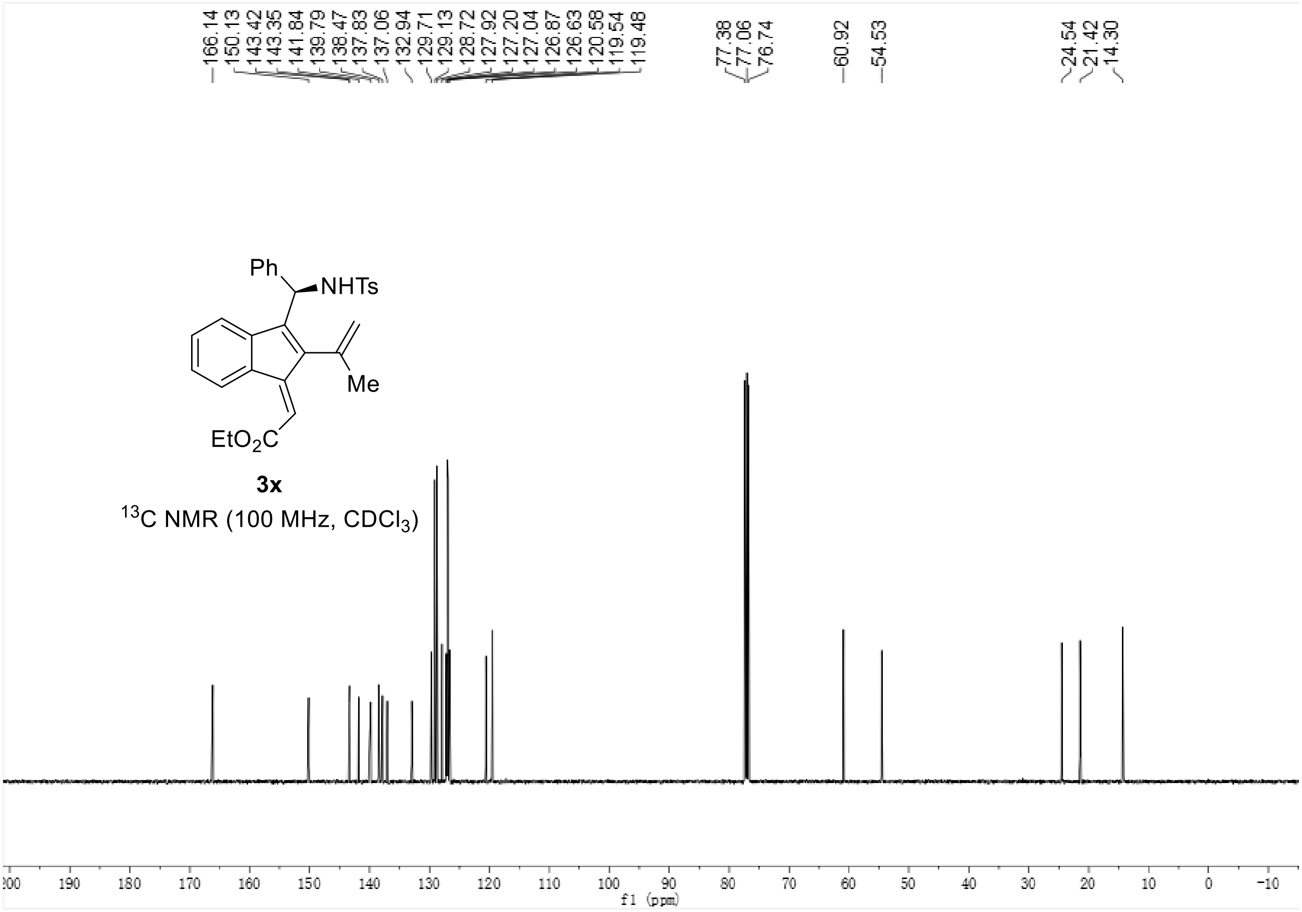
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{32}H_{27}NO_2SNa^+$ 512.1655



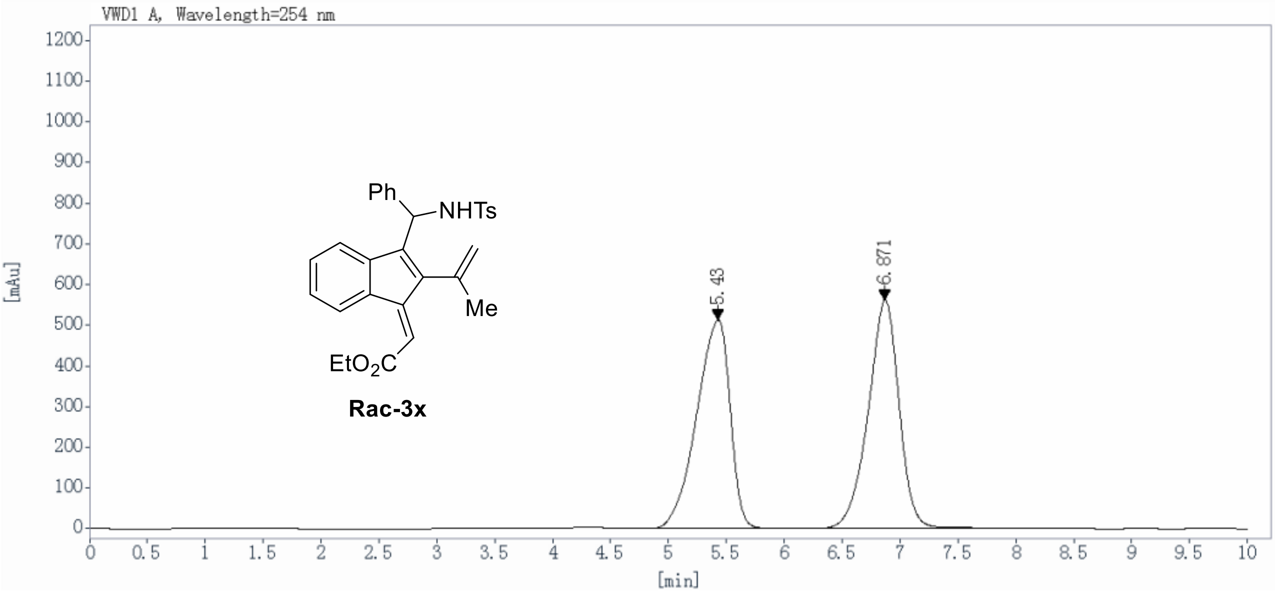
**3x**

$^1H$ NMR (400 MHz, $CDCl_3$)

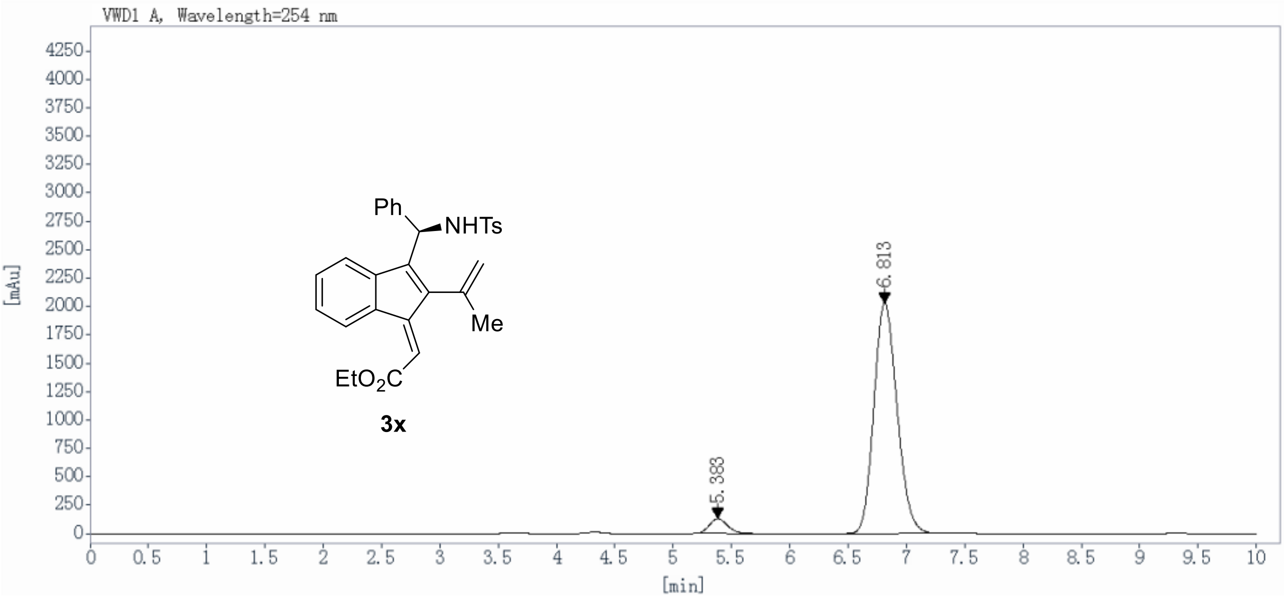


**3x**

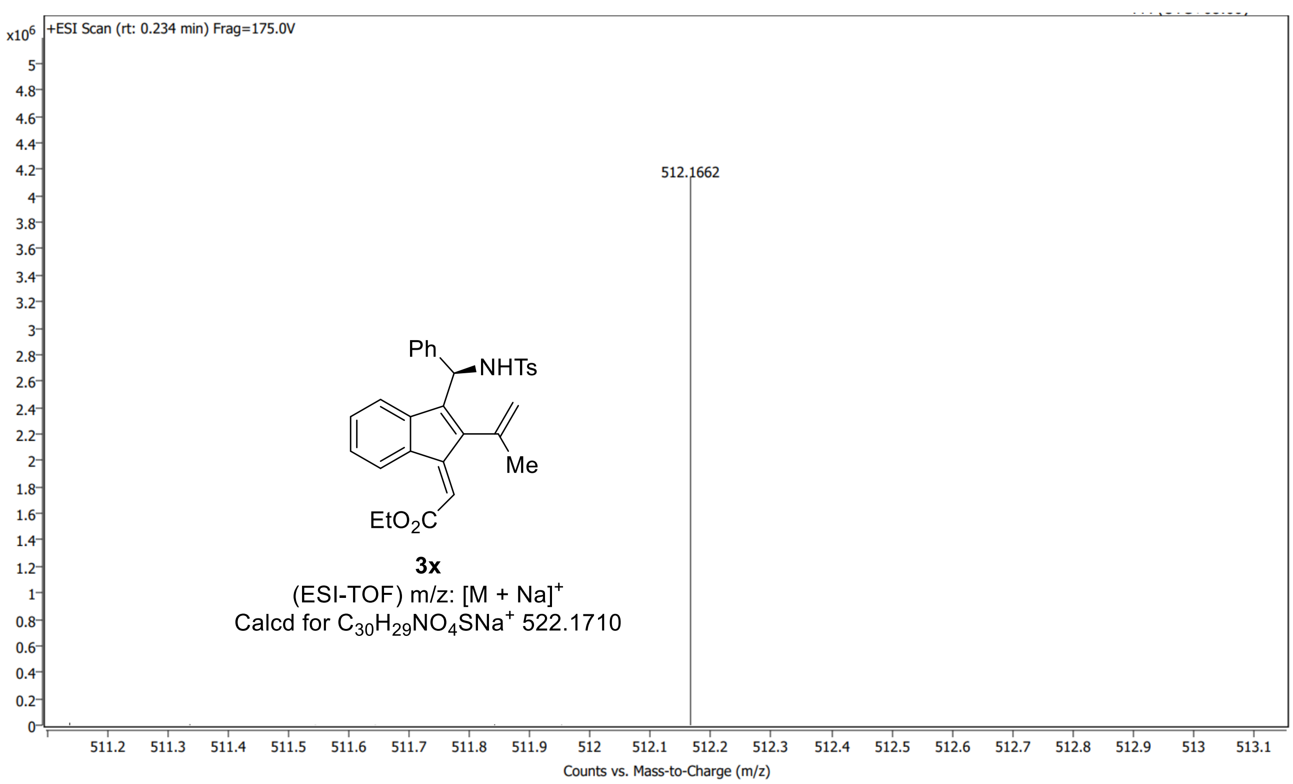
$^{13}C$ NMR (100 MHz, $CDCl_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.430 | BB | 0.32 | 512.0977 | 10317.1680 | 49.5579 |
| 6.871 | BV R | 0.28 | 562.8331 | 10501.2432 | 50.4421 |
| | | | Totals: | 20818.4111 | 100.0000 |



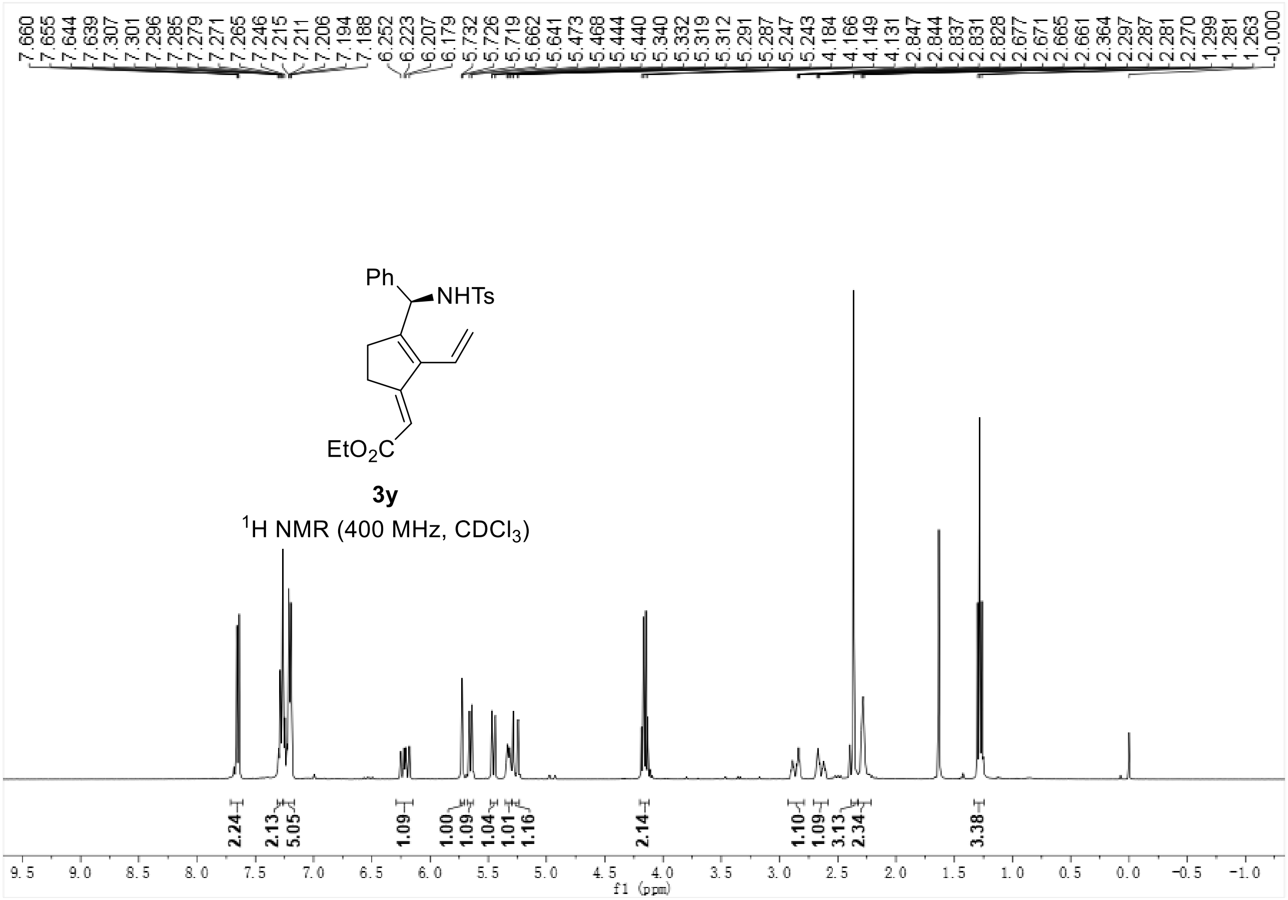
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.383 | BBA | 0.17 | 126.9306 | 1338.8942 | 4.5453 |
| 6.813 | BBA | 0.22 | 2031.9143 | 28117.7168 | 95.4547 |
| | | | Totals: | 29456.6110 | 100.0000 |

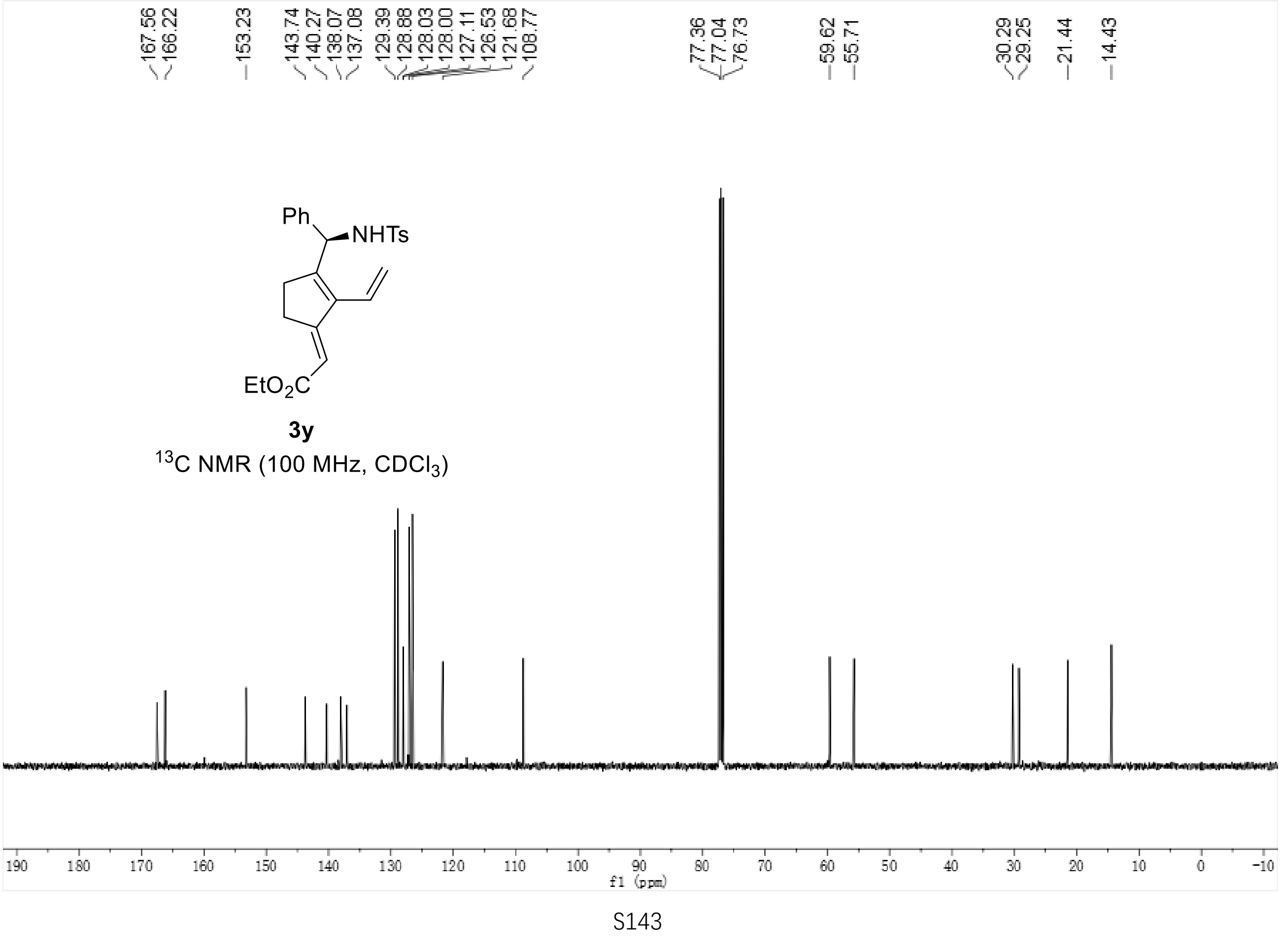


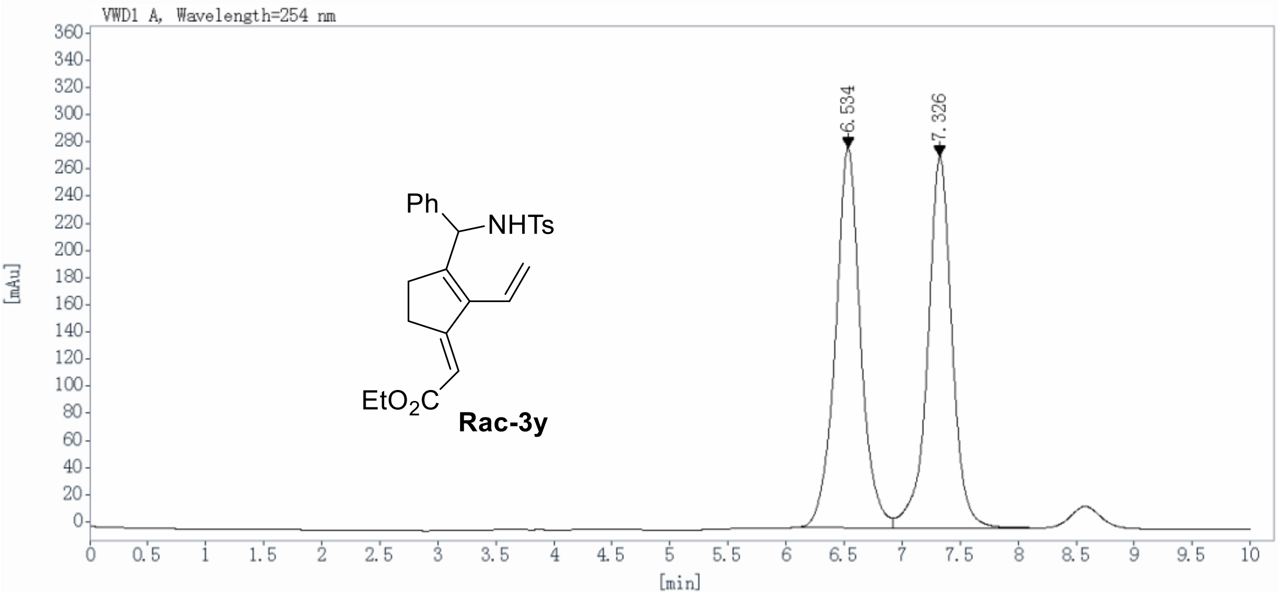
**3x**

(ESI-TOF) m/z: $[M + Na]^+$

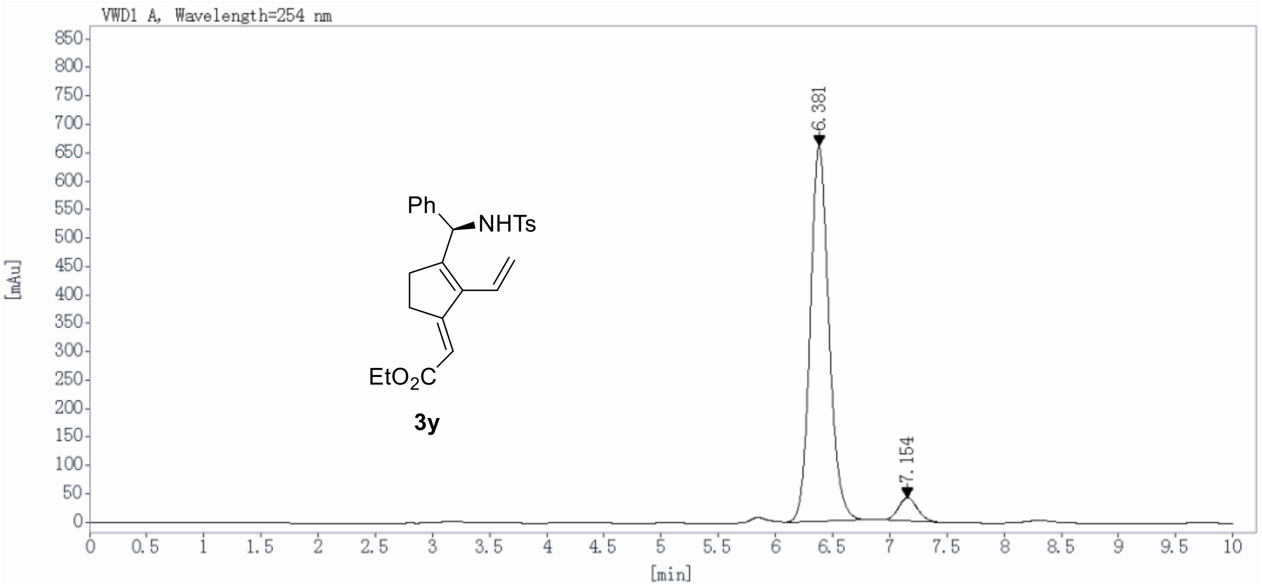
Calcd for $C_{30}H_{29}NO_4SNa^+$ 522.1710


7.660 7.655 7.644 7.639 7.307 7.301 7.296 7.285 7.279 7.271 7.265 7.246 7.215 7.211 7.206 7.194 7.188 6.252 6.223 6.207 6.179 5.732 5.726 5.719 5.662 5.641 5.473 5.468 5.444 5.440 5.340 5.332 5.319 5.312 5.291 5.287 5.247 5.243 4.184 4.166 4.149 4.131 2.847 2.844 2.837 2.831 2.828 2.677 2.671 2.665 2.661 2.364 2.297 2.287 2.281 2.270 1.299 1.281 1.263 -0.000
Ph
NHTs
EtO2C
3y
1H NMR (400 MHz, CDCl3)
2.24 2.13 5.05 1.09 1.00 1.09 1.04 1.01 1.16 2.14 1.10 1.09 3.13 2.34 3.38
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

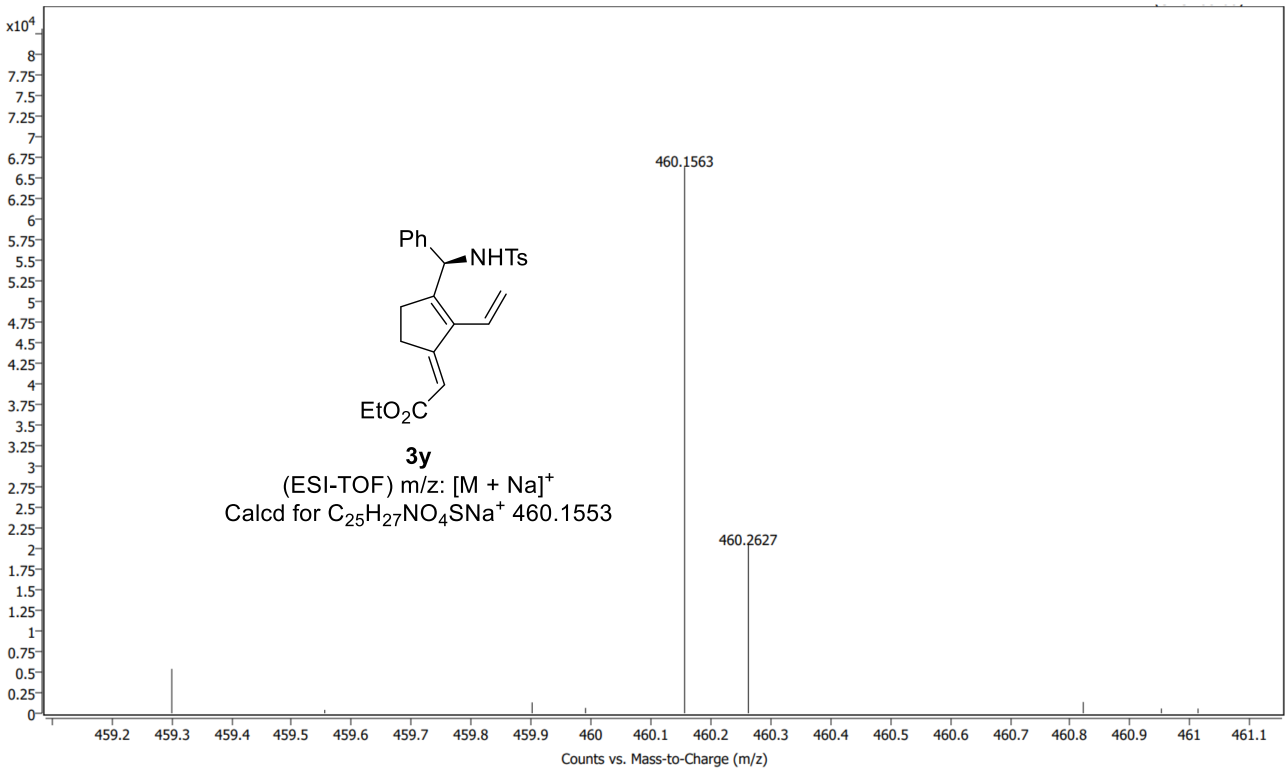

167.56 166.22 153.23 143.74 140.27 138.07 137.08 129.39 128.88 128.03 128.00 127.11 126.53 121.68 108.77 77.36 77.04 76.73 59.62 55.71 30.29 29.25 21.44 14.43
Ph
NHTs
EtO2C
3y
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.534 | BV | 0.22 | 279.9293 | 4222.8760 | 51.3858 |
| 7.326 | VV R | 0.22 | 273.8208 | 3995.1094 | 48.6142 |
| | | | Totals: | 8217.9854 | 100.0000 |



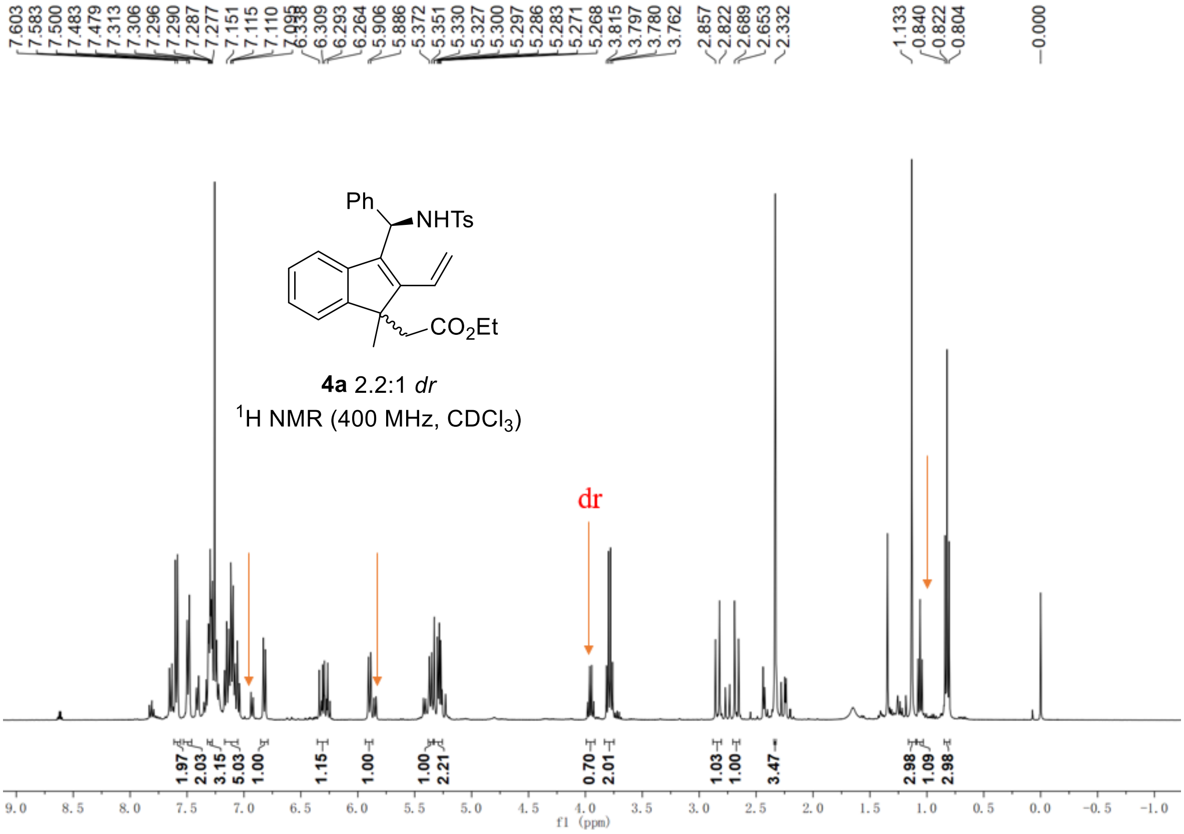
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.381 | BB | 0.17 | 660.3036 | 7509.8140 | 94.0707 |
| 7.154 | BBA | 0.18 | 40.9977 | 473.3452 | 5.9293 |
| | | | Totals: | 7983.1591 | 100.0000 |



**3y**

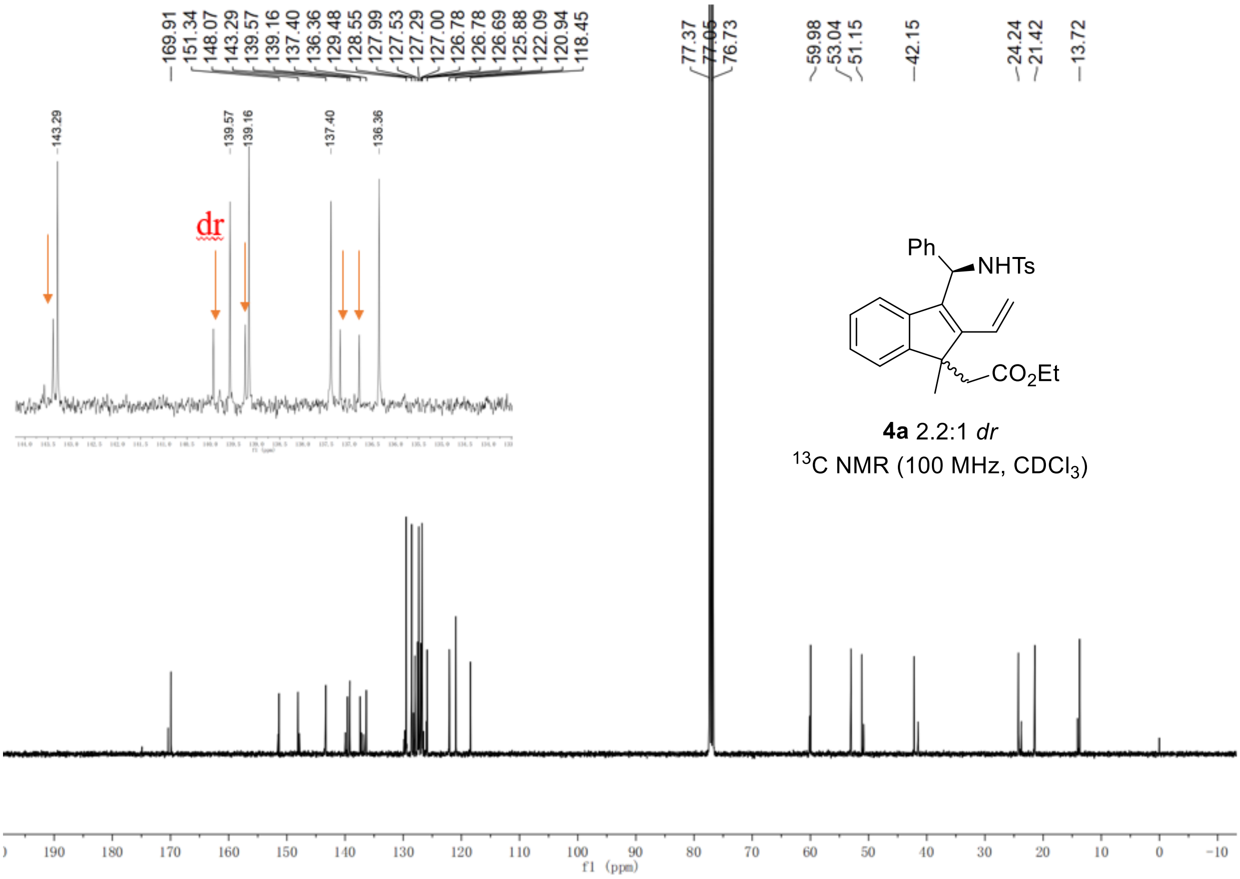
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{25}H_{27}NO_4SNa^+$ 460.1553



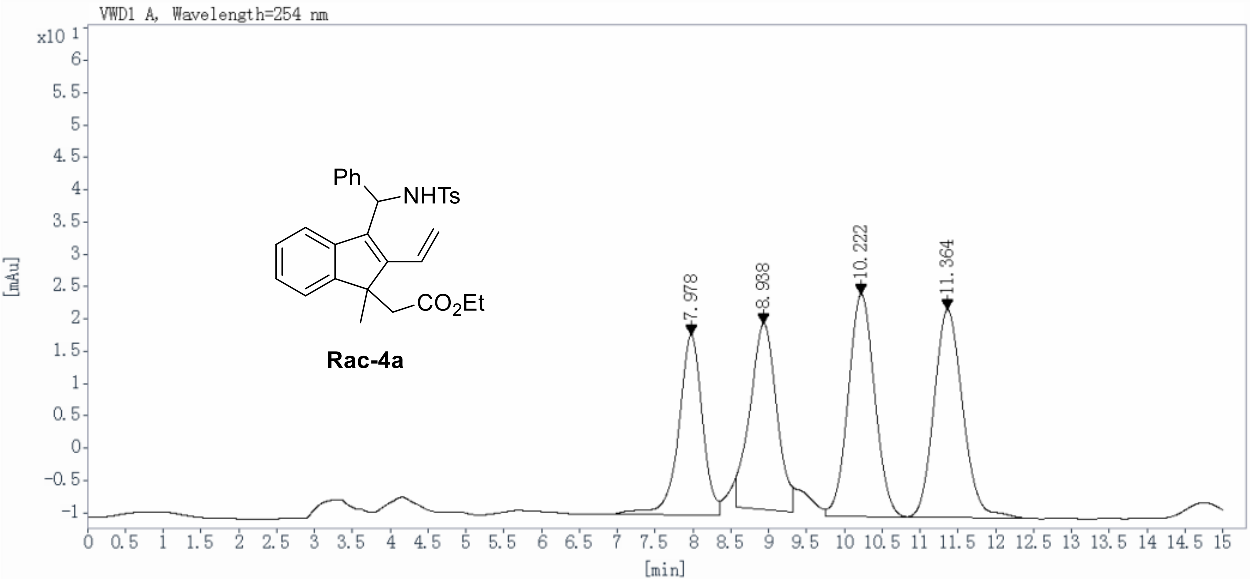
**4a** 2.2:1 *dr*

$^1$H NMR (400 MHz, $CDCl_3$)



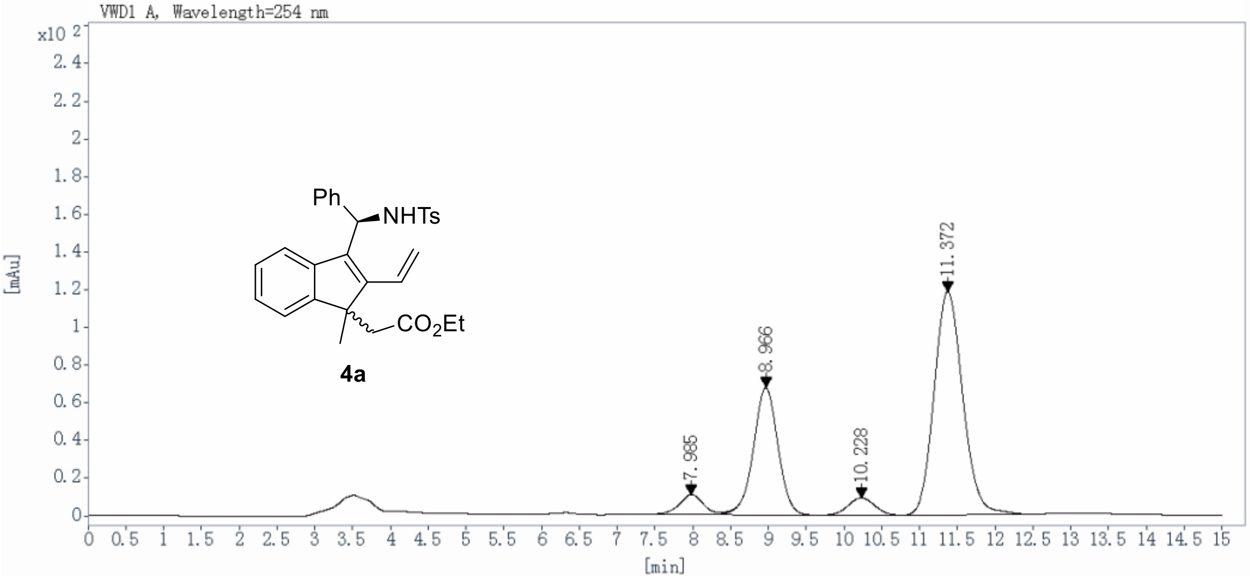
**4a** 2.2:1 *dr*

$^{13}$C NMR (100 MHz, $CDCl_3$)



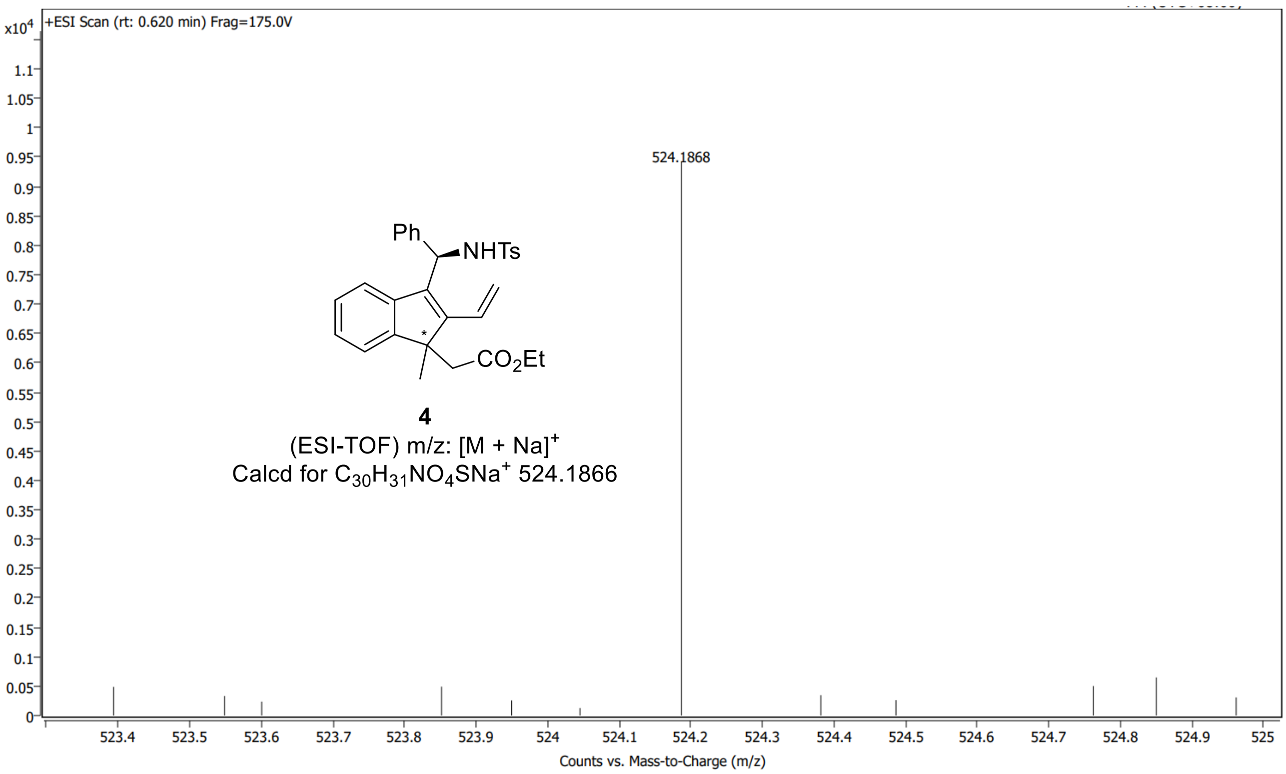
**Rac-4a**

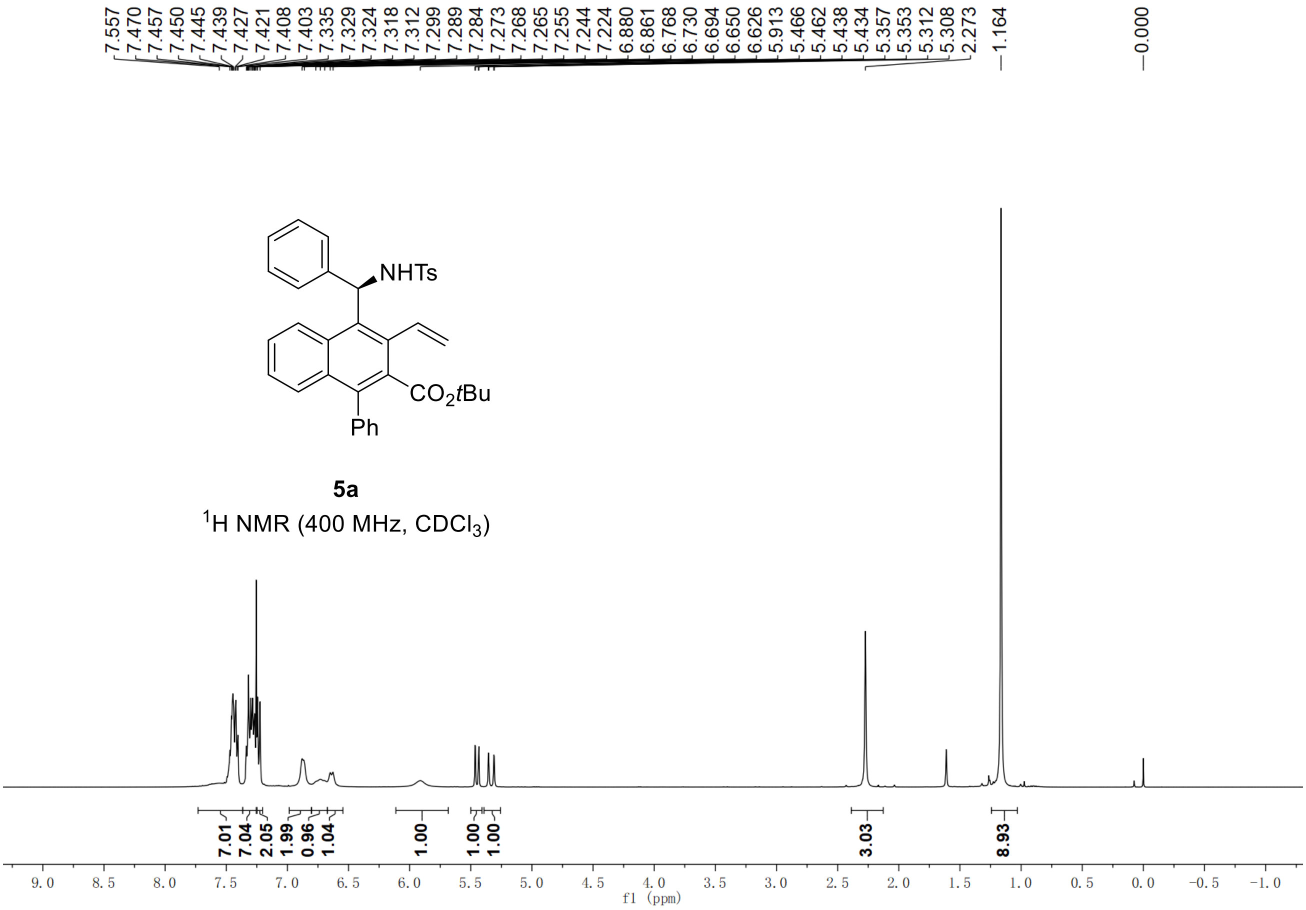
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.978 | BV | 0.33 | 27.8856 | 609.8063 | 20.3173 |
| 8.938 | MM | 0.41 | 28.7505 | 703.4449 | 23.4371 |
| 10.222 | VB | 0.38 | 34.4102 | 837.0250 | 27.8877 |
| 11.364 | BB | 0.41 | 32.1978 | 851.1353 | 28.3578 |
|  |  |  | Totals: | 3001.4116 | 100.0000 |



**4a**

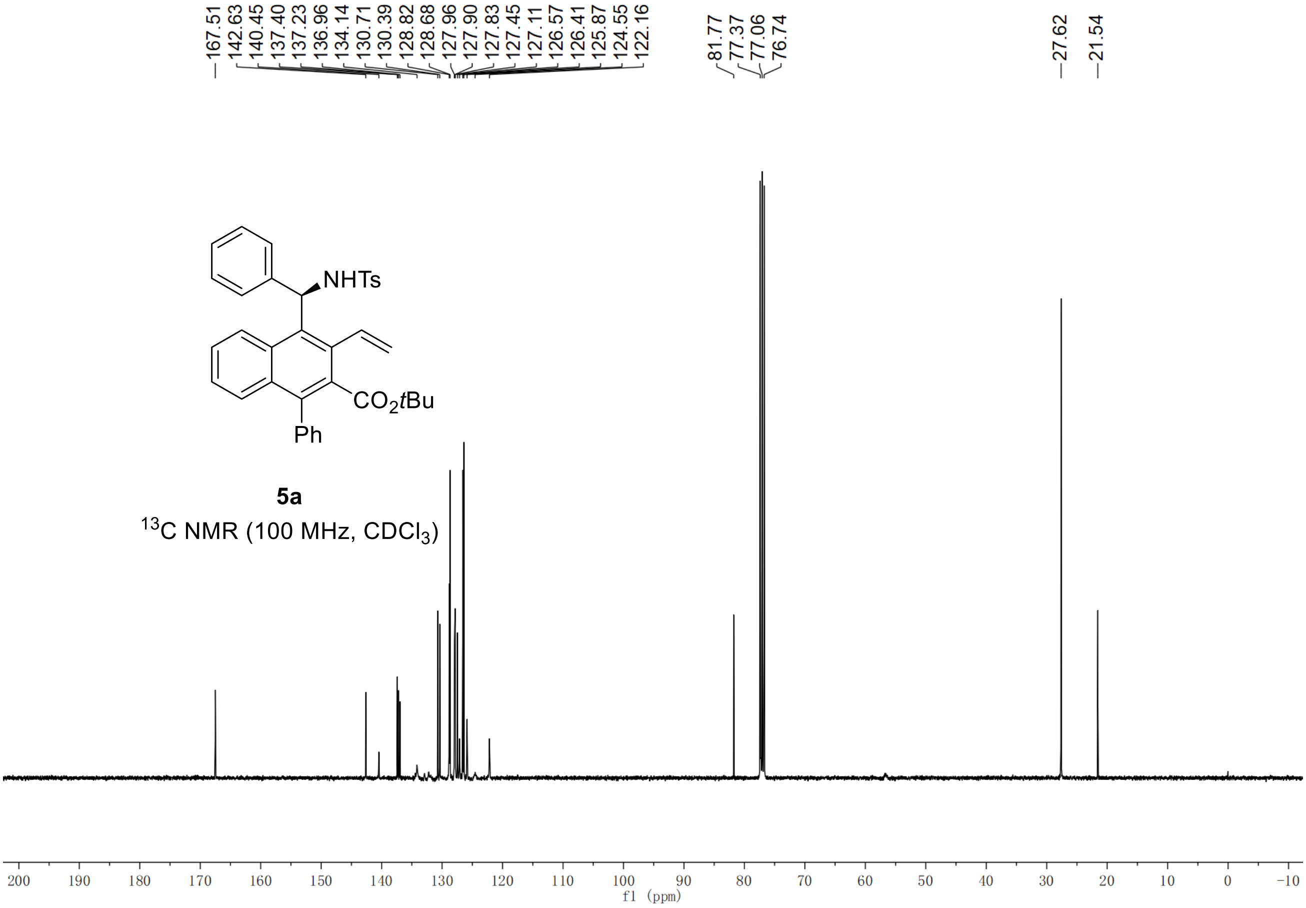
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.985 | BV E | 0.34 | 10.5819 | 236.0215 | 4.6193 |
| 8.966 | VB R | 0.35 | 67.6809 | 1533.2036 | 30.0071 |
| 10.228 | BB | 0.38 | 9.1286 | 221.6095 | 4.3372 |
| 11.372 | BB | 0.41 | 118.5133 | 3118.6306 | 61.0363 |
|  |  |  | Totals: | 5109.4652 | 100.0000 |


x10^4
+ESI Scan (rt: 0.620 min) Frag=175.0V
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
524.1868
Ph
NHTs
*
CO2Et
4
(ESI-TOF) m/z: [M + Na]+
Calcd for C30H31NO4SNa+ 524.1866
523.4
523.5
523.6
523.7
523.8
523.9
524
524.1
524.2
524.3
524.4
524.5
524.6
524.7
524.8
524.9
525
Counts vs. Mass-to-Charge (m/z)



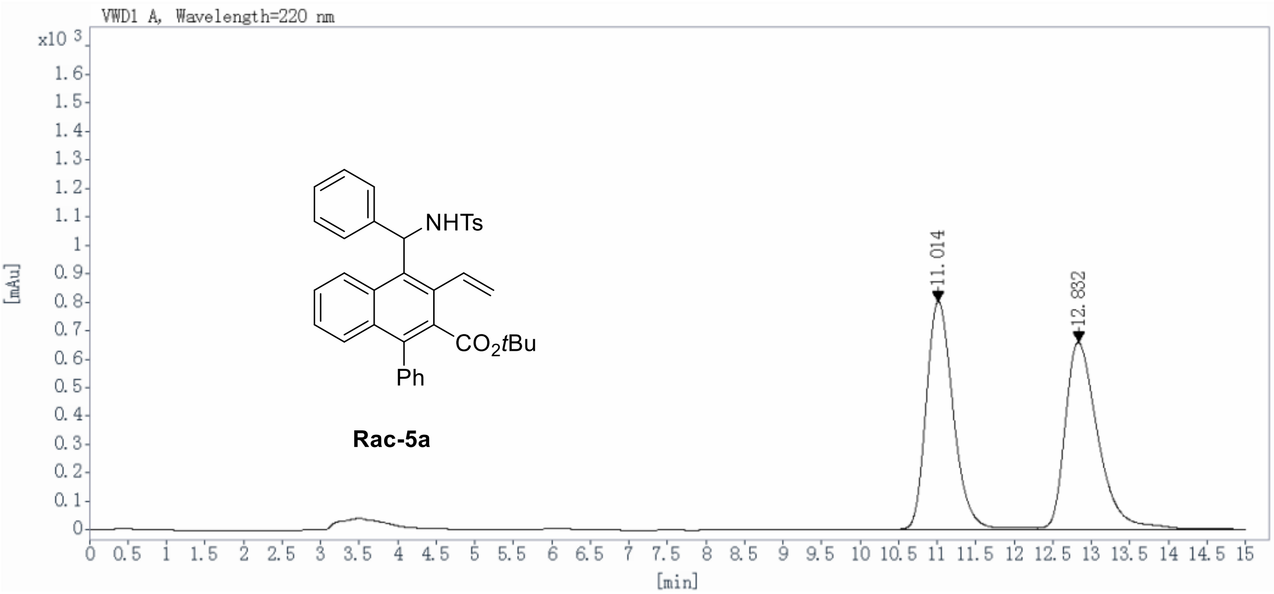
**5a**

$^1$H NMR (400 MHz, CDCl$_3$)



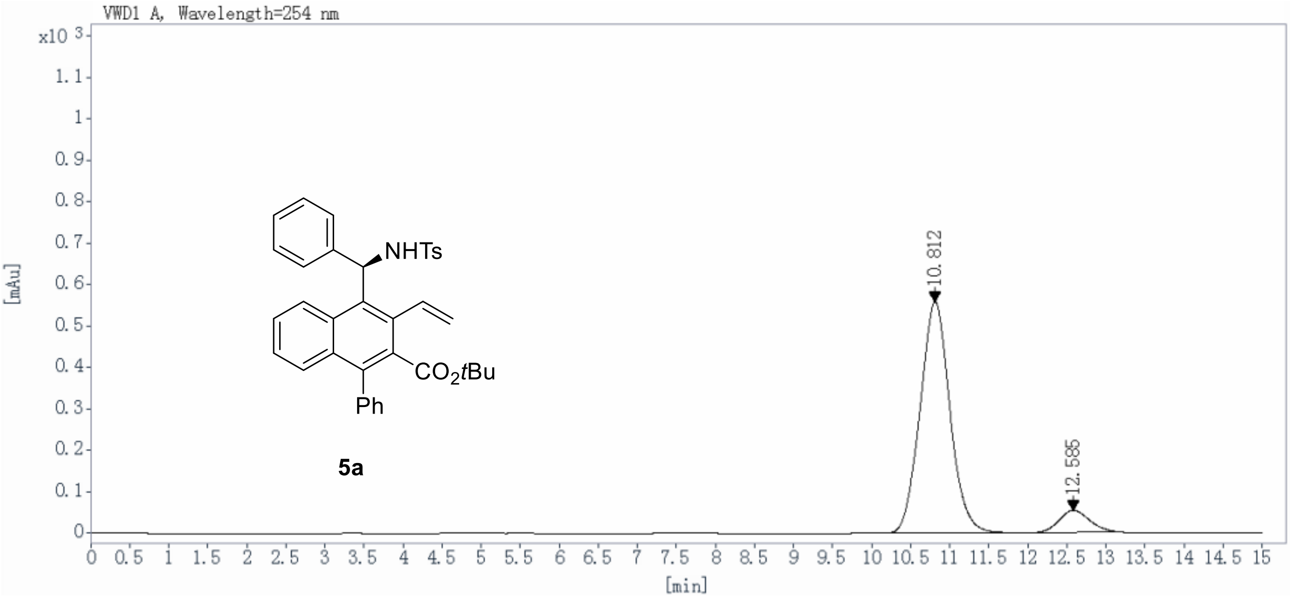
**5a**

$^{13}$C NMR (100 MHz, CDCl$_3$)



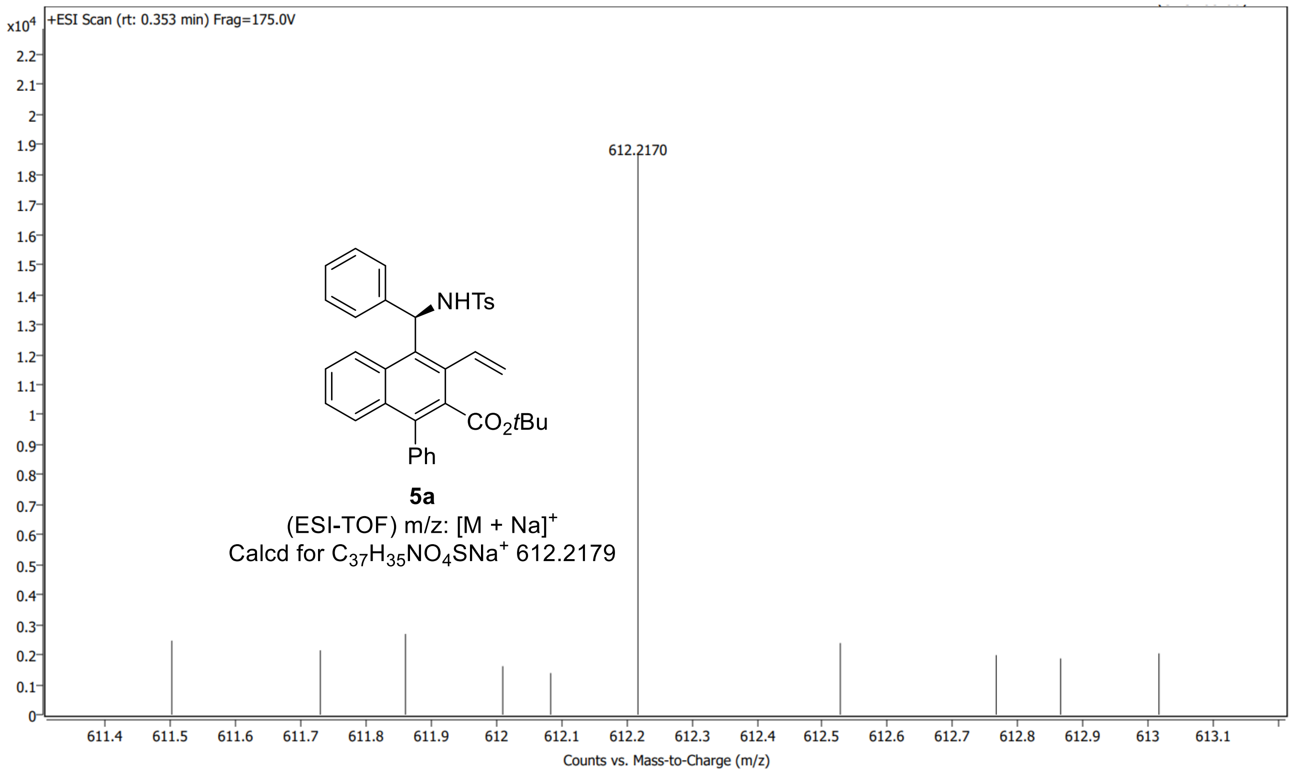
**Rac-5a**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 11.014 | BV R | 0.38 | 802.5752 | 19586.8789 | 50.0500 |
| 12.832 | VV R | 0.45 | 657.7418 | 19547.7578 | 49.9500 |
|  |  |  | Totals: | 39134.6367 | 100.0000 |



**5a**

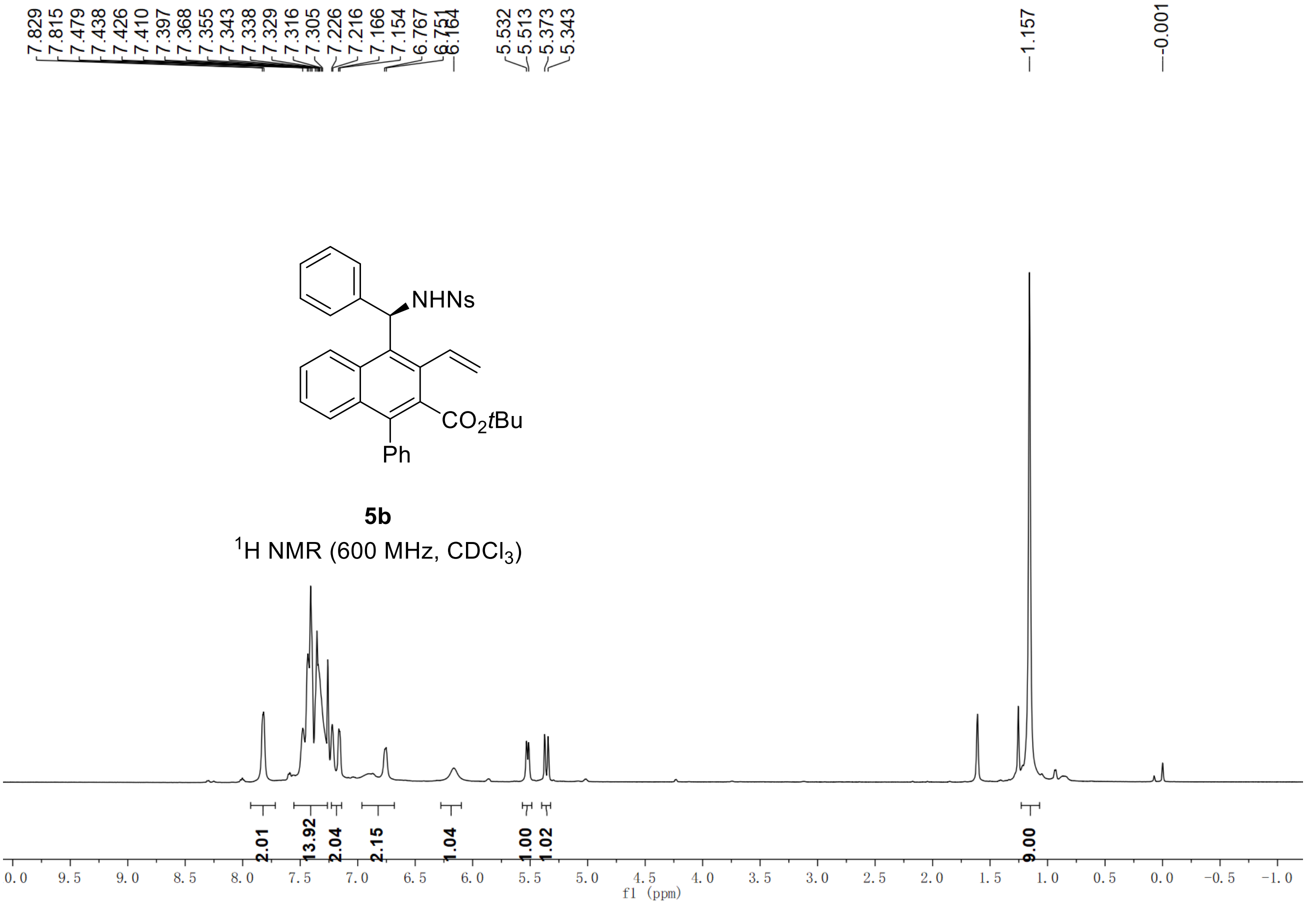
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 10.812 | BBA | 0.40 | 557.9377 | 14832.0020 | 91.1894 |
| 12.585 | BBA | 0.42 | 52.9944 | 1433.0531 | 8.8106 |
|  |  |  | Totals: | 16265.0551 | 100.0000 |



**5a**

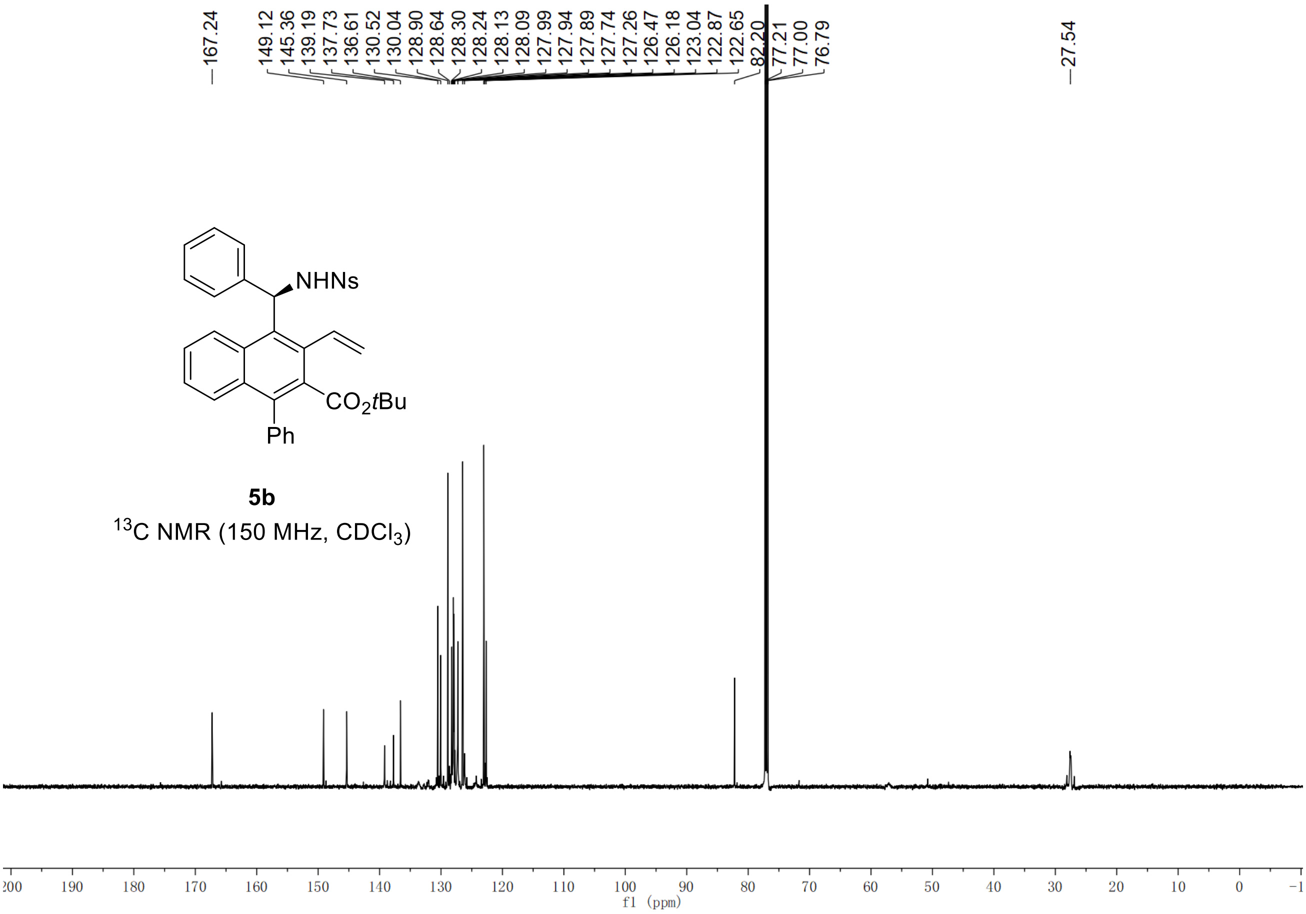
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{37}H_{35}NO_4SNa^+$ 612.2179



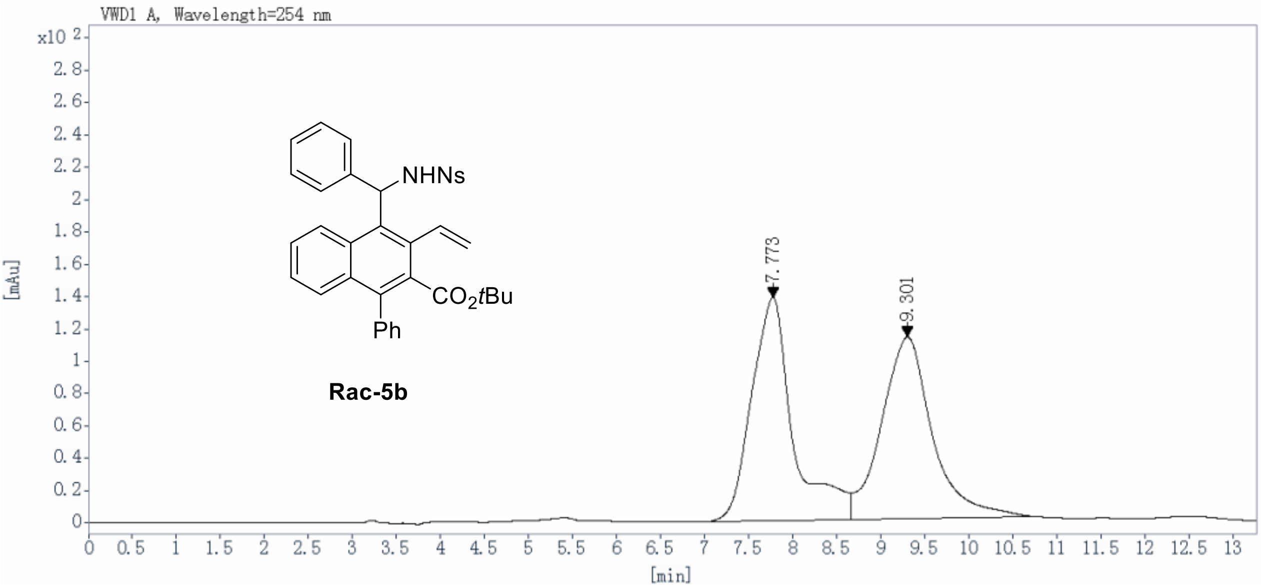
**5b**

$^1$H NMR (600 MHz, CDCl$_3$)



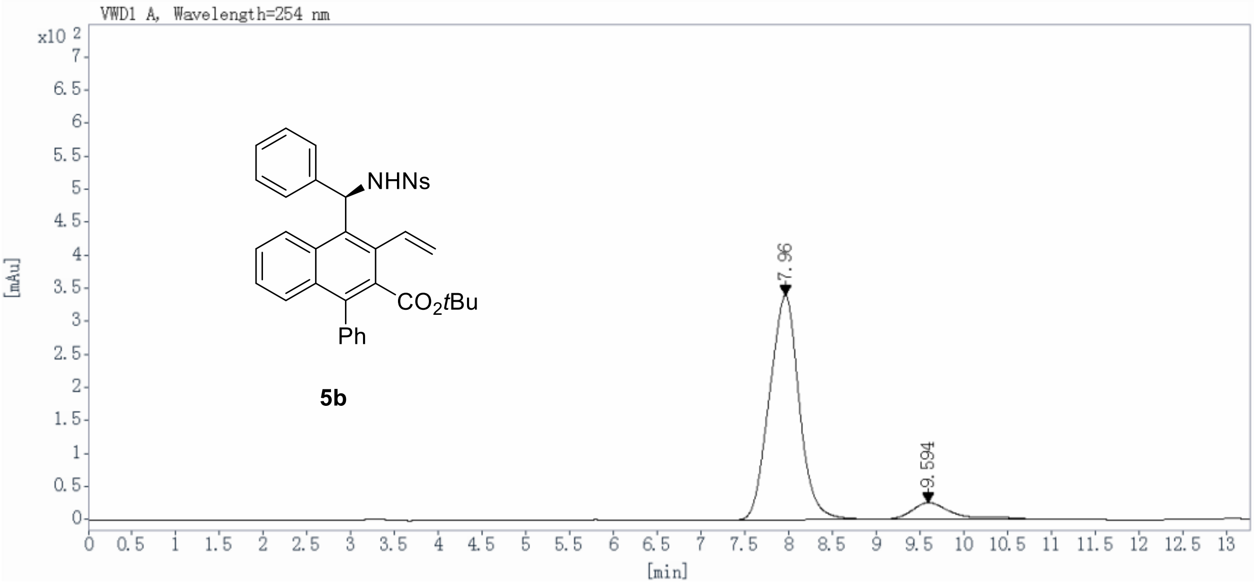
**5b**

$^{13}$C NMR (150 MHz, CDCl$_3$)



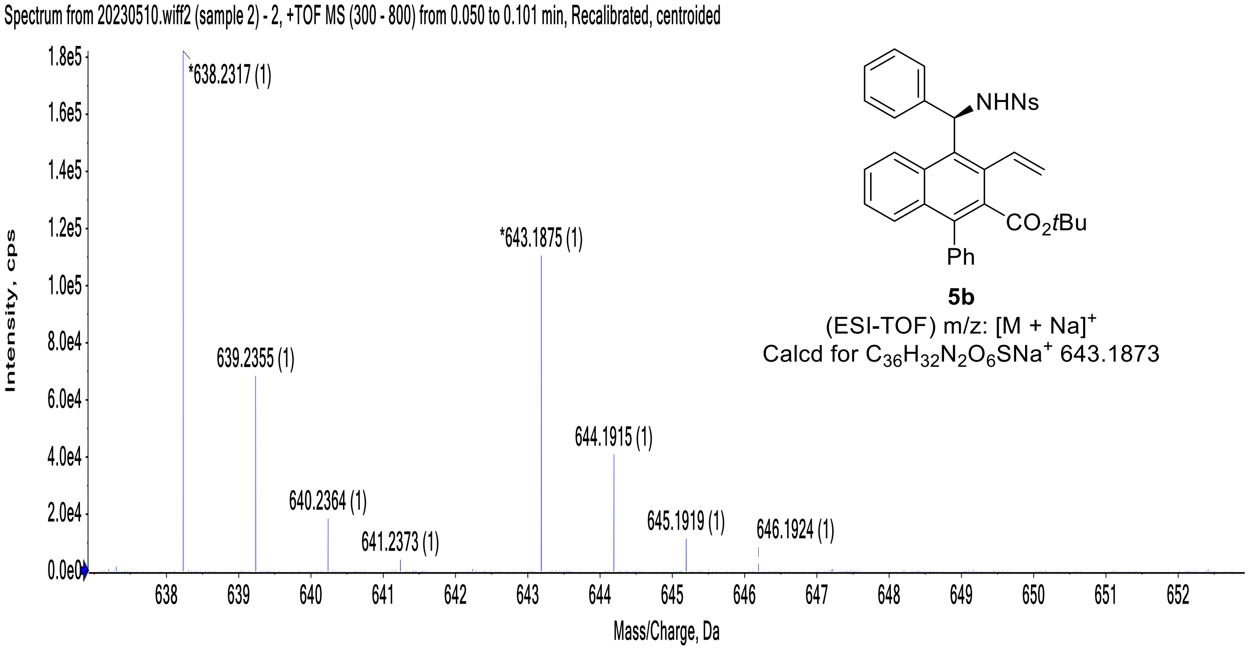
**Rac-5b**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.773 | BV R | 0.48 | 138.1967 | 4531.0581 | 50.2714 |
| 9.301 | VBA | 0.61 | 112.2253 | 4482.1289 | 49.7286 |
| | | | Totals: | 9013.1870 | 100.0000 |



**5b**

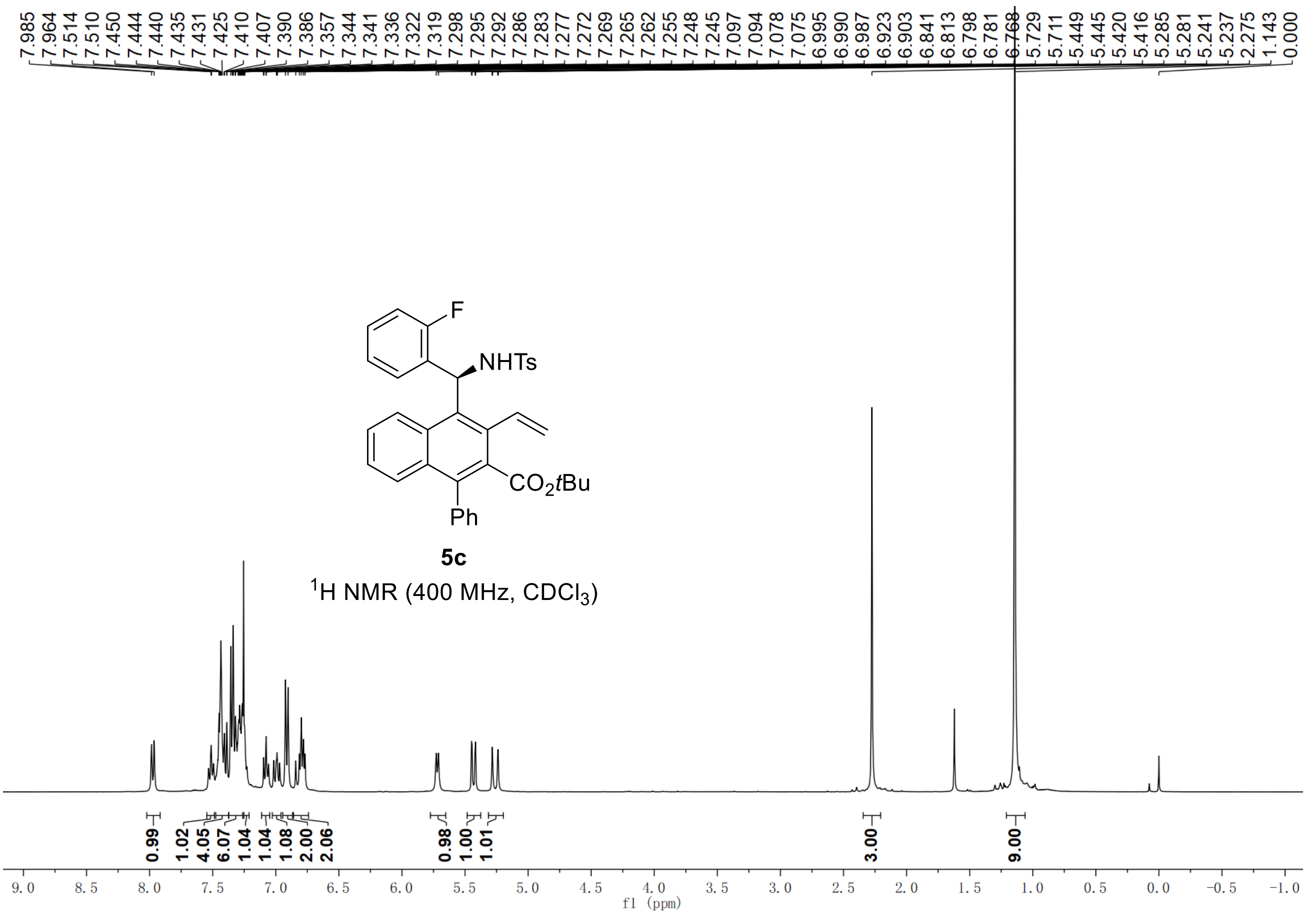
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.960 | BV | 0.38 | 340.1908 | 8038.5566 | 91.1440 |
| 9.594 | VV R | 0.46 | 25.1141 | 781.0633 | 8.8560 |
| | | | Totals: | 8819.6199 | 100.0000 |



**5b**

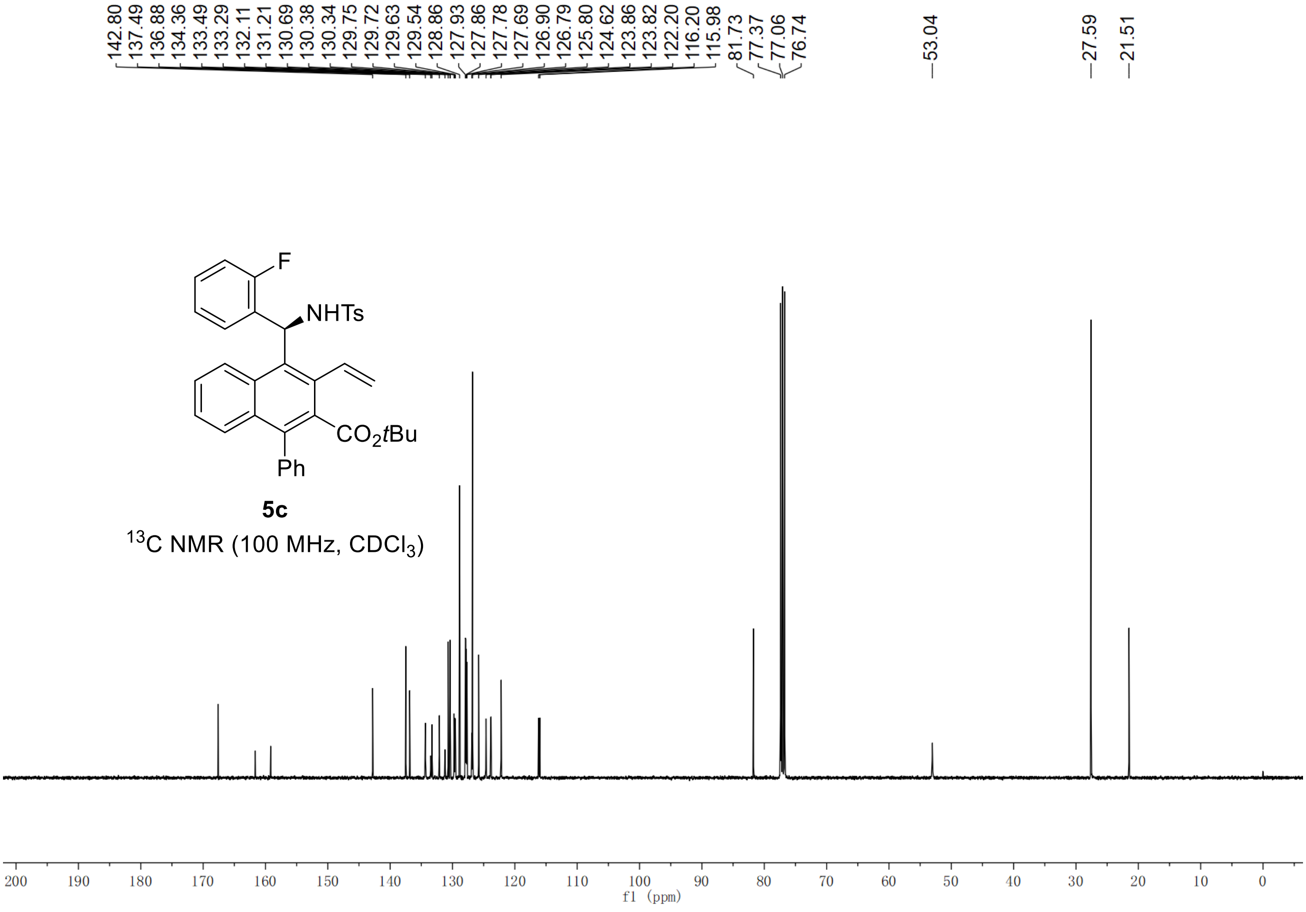
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{36}H_{32}N_2O_6SNa^+$ 643.1873



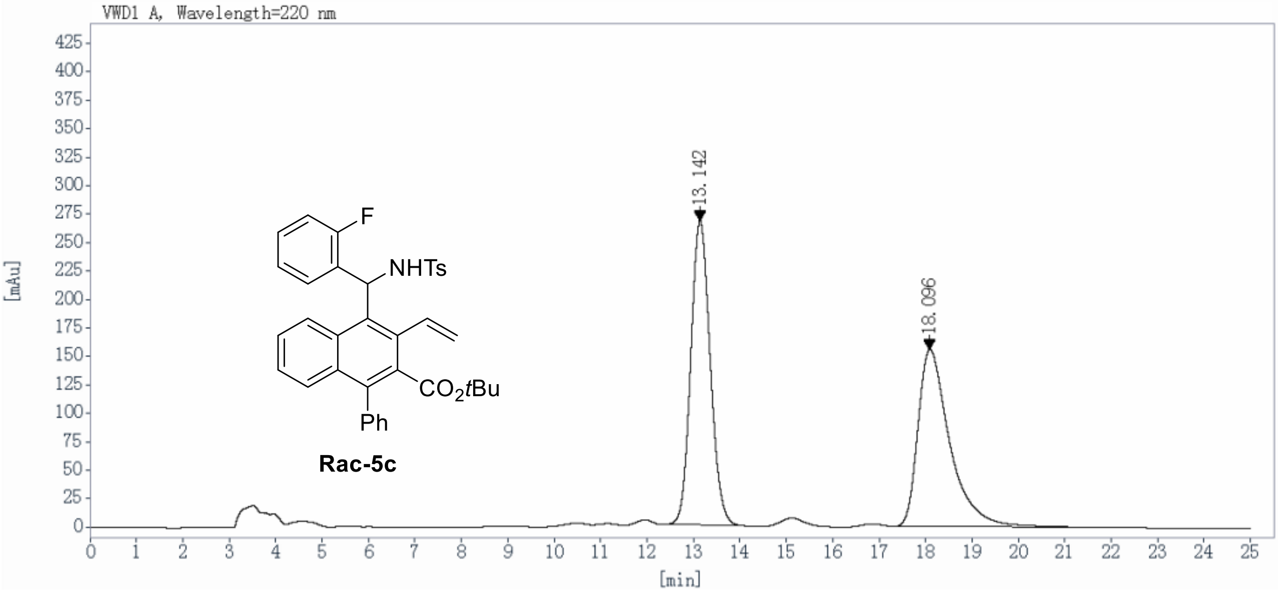
**5c**

$^1$H NMR (400 MHz, CDCl$_3$)

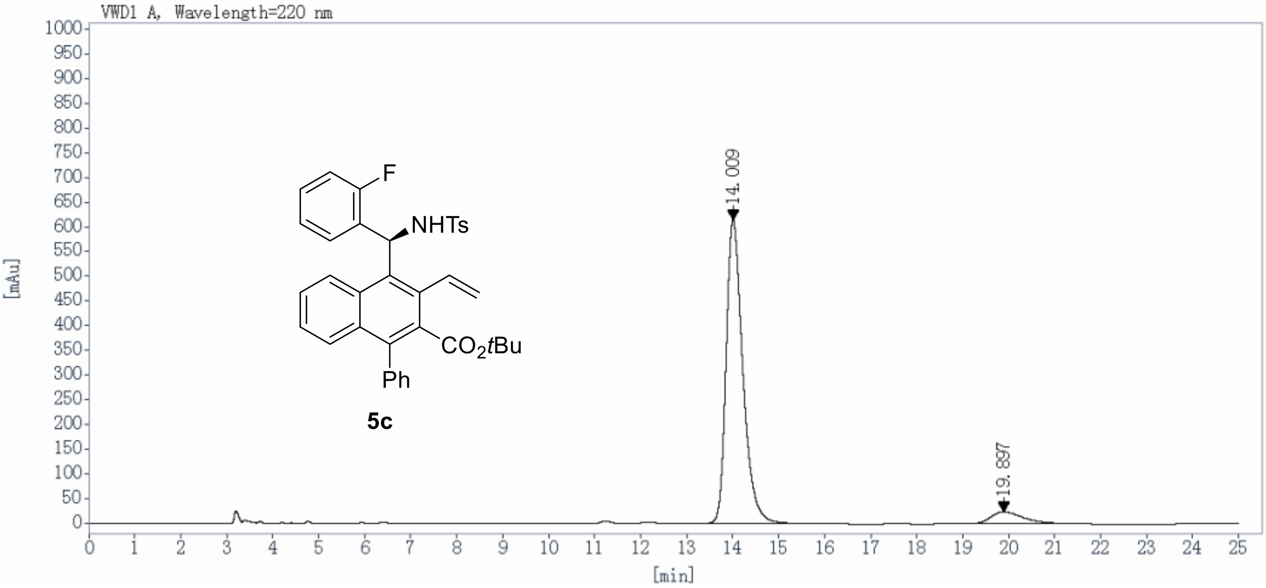


**5c**

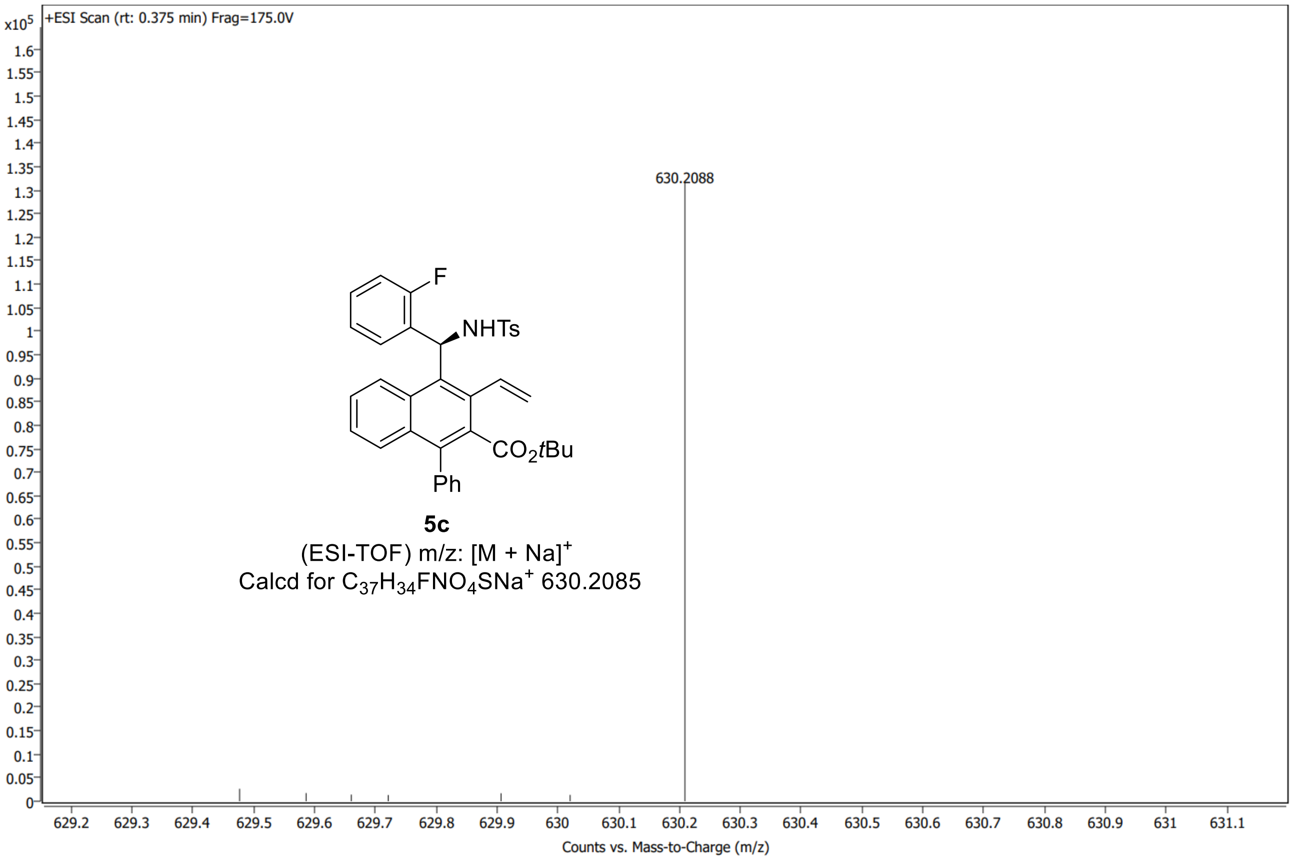
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 13.142 | BBA | 0.45 | 266.9952 | 7741.9546 | 50.8511 |
| 18.096 | BB | 0.72 | 155.7985 | 7482.8101 | 49.1489 |
| | | | Totals: | 15224.7646 | 100.0000 |



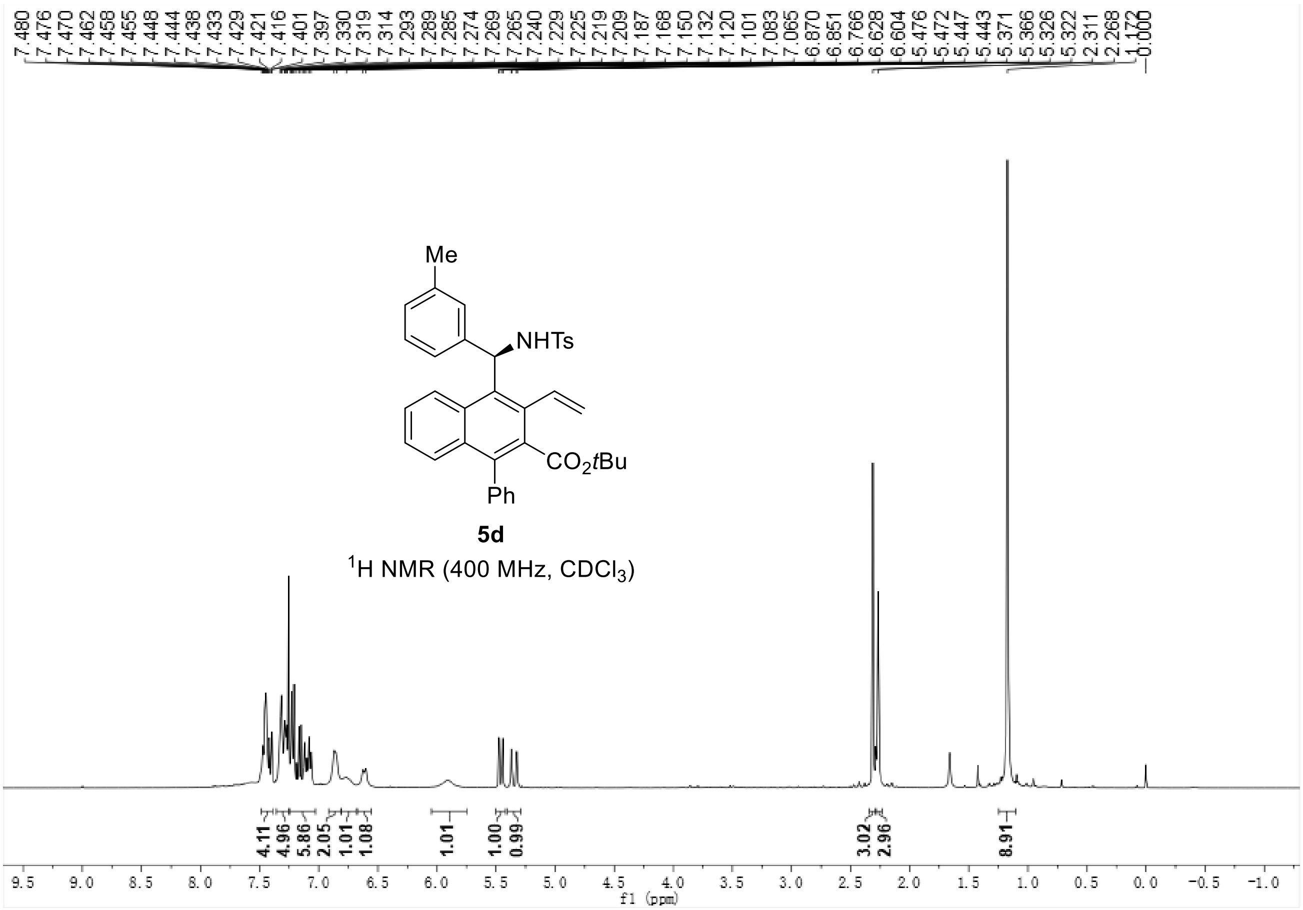
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 14.009 | BBA | 0.38 | 614.4079 | 15505.8672 | 92.9166 |
| 19.897 | BBA | 0.74 | 24.1404 | 1182.0822 | 7.0834 |
| | | | Totals: | 16687.9493 | 100.0000 |



**5c**

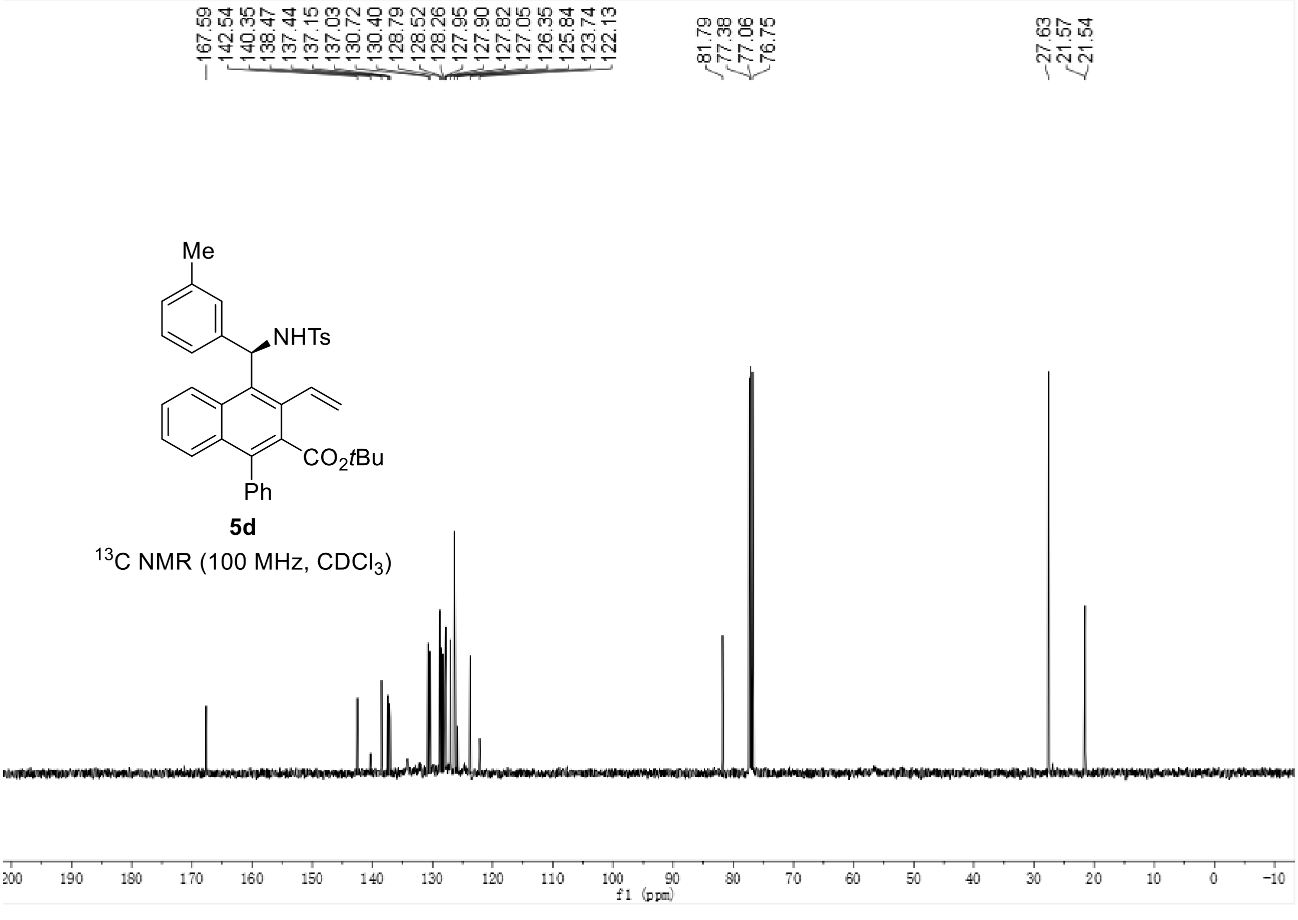
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{37}H_{34}FNO_4SNa^+$ 630.2085



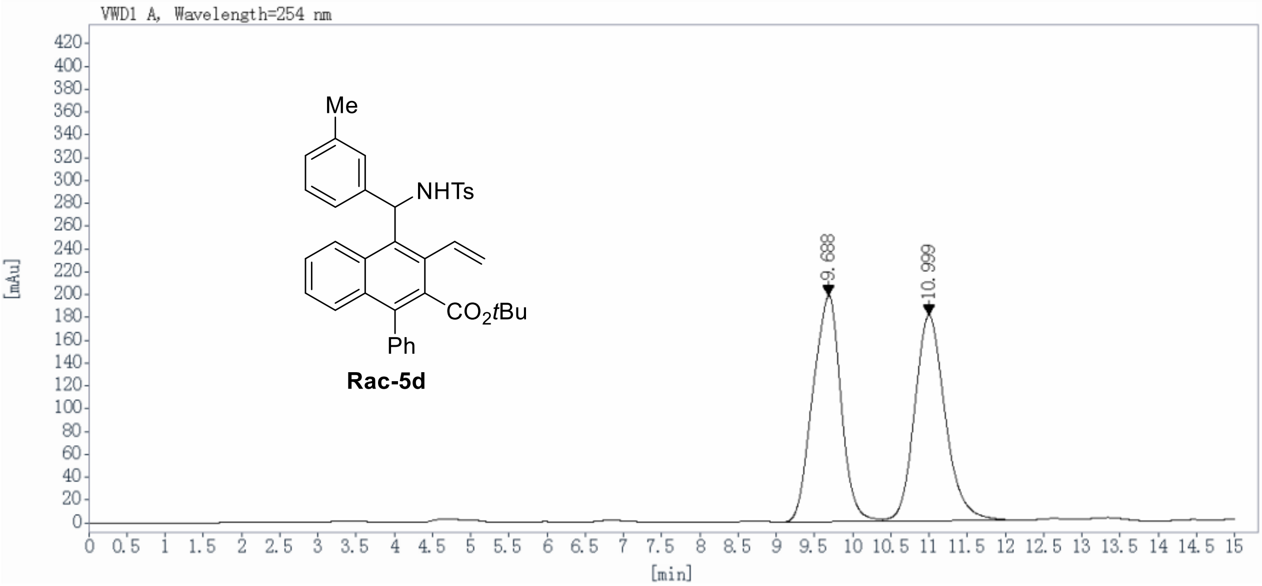
**5d**

$^1$H NMR (400 MHz, CDCl$_3$)



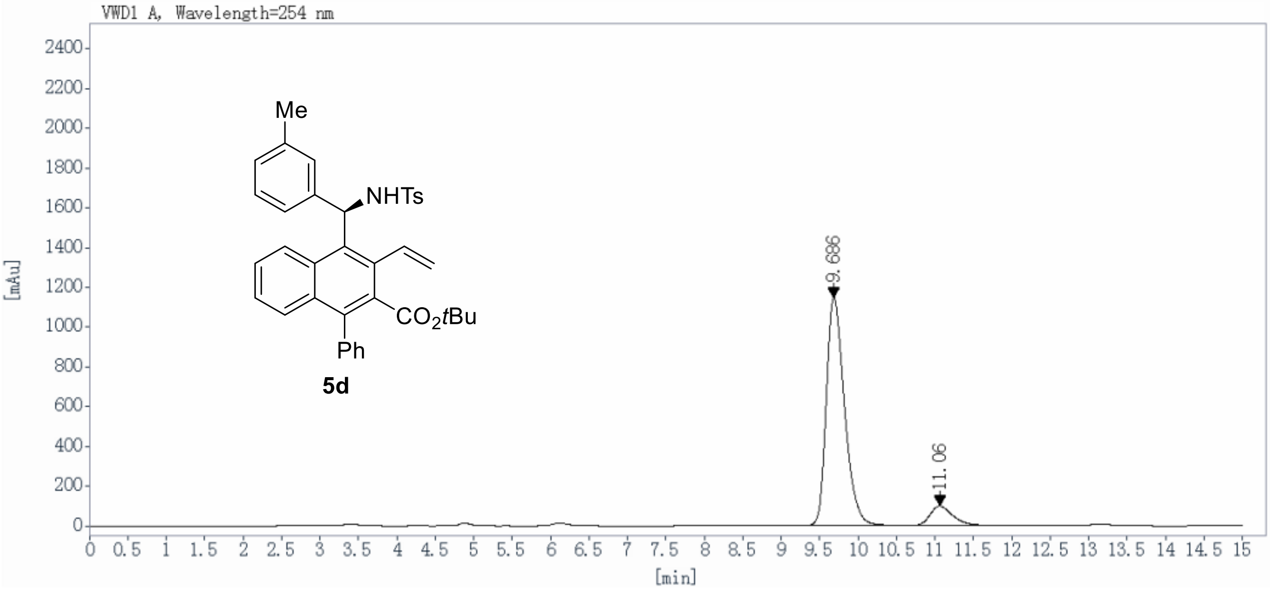
**5d**

$^{13}$C NMR (100 MHz, CDCl$_3$)



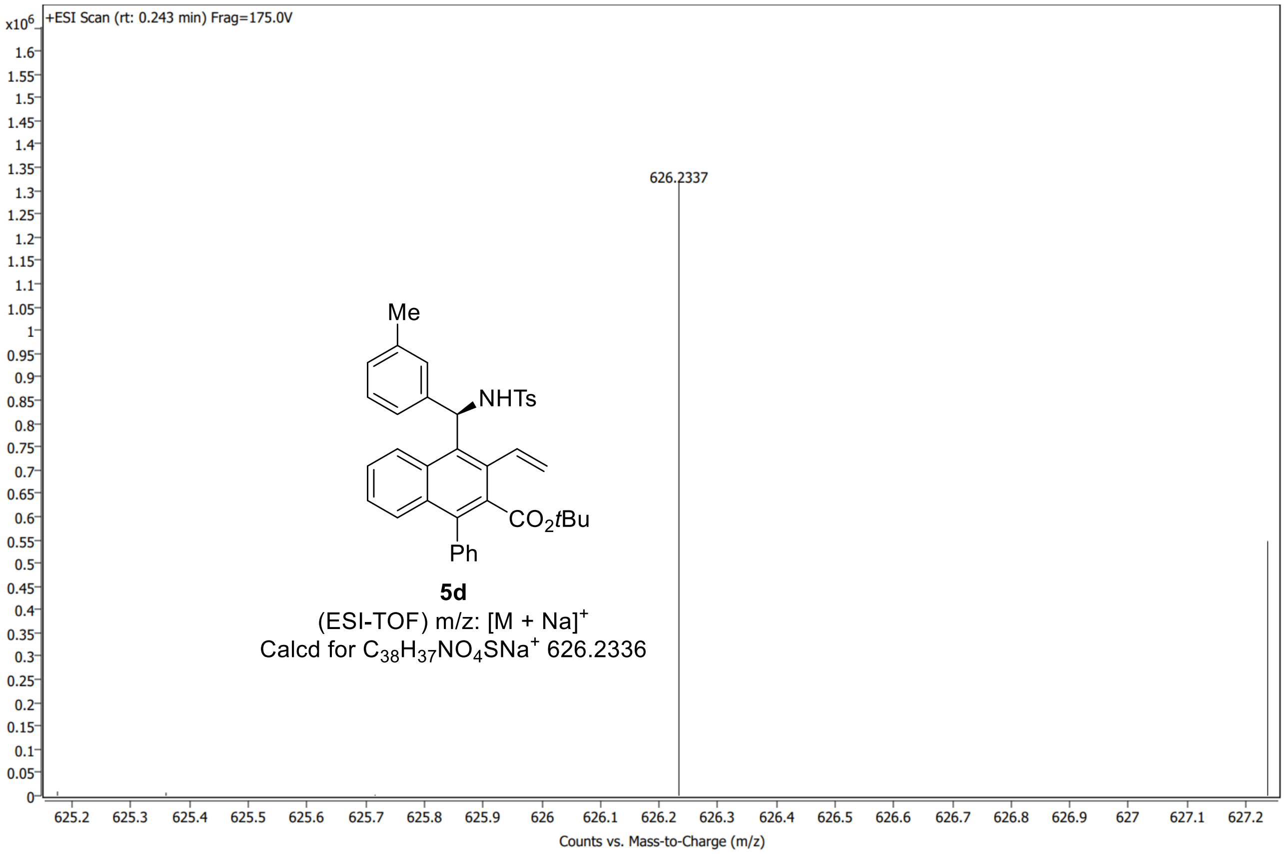
**Rac-5d**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.688 | BV | 0.42 | 198.1110 | 5079.8975 | 50.2752 |
| 10.999 | VB | 0.43 | 180.4312 | 5024.2783 | 49.7248 |
|  |  |  | Totals: | 10104.1758 | 100.0000 |



**5d**

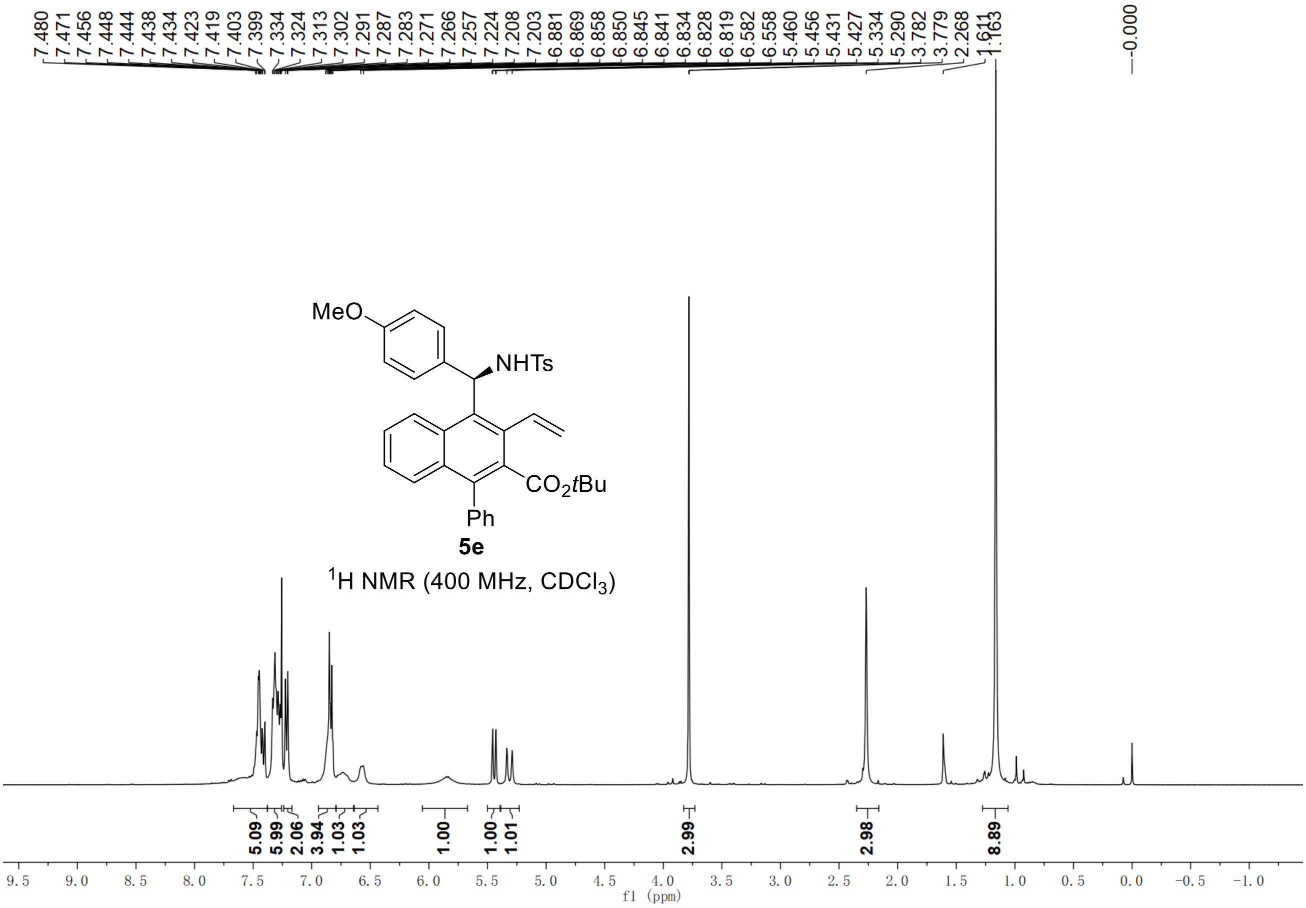
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.686 | BBA | 0.25 | 1149.2441 | 18818.1953 | 90.6083 |
| 11.060 | BBA | 0.31 | 96.6658 | 1950.5299 | 9.3917 |
|  |  |  | Totals: | 20768.7252 | 100.0000 |



**5d**

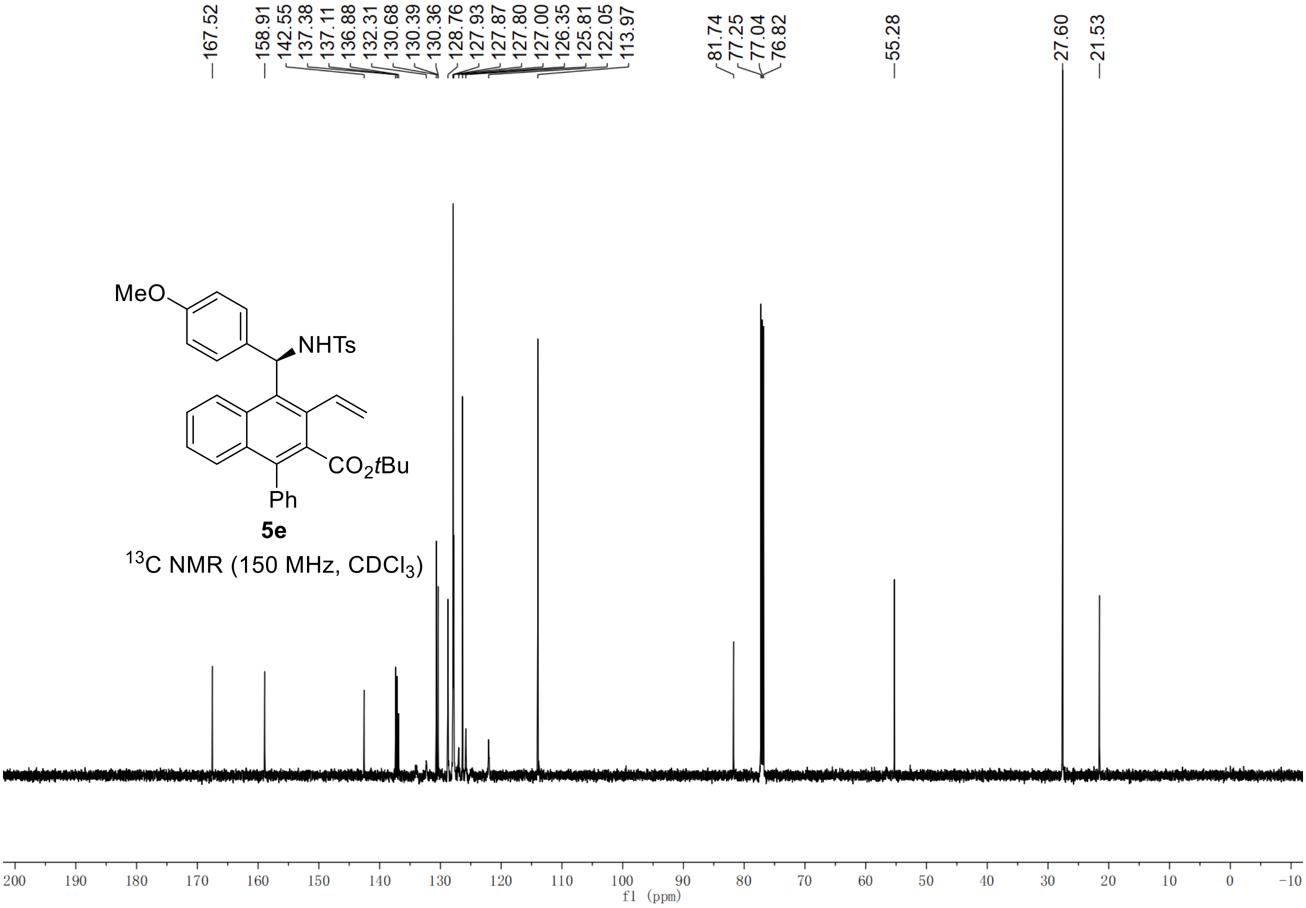
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{38}H_{37}NO_4SNa^+$ 626.2336



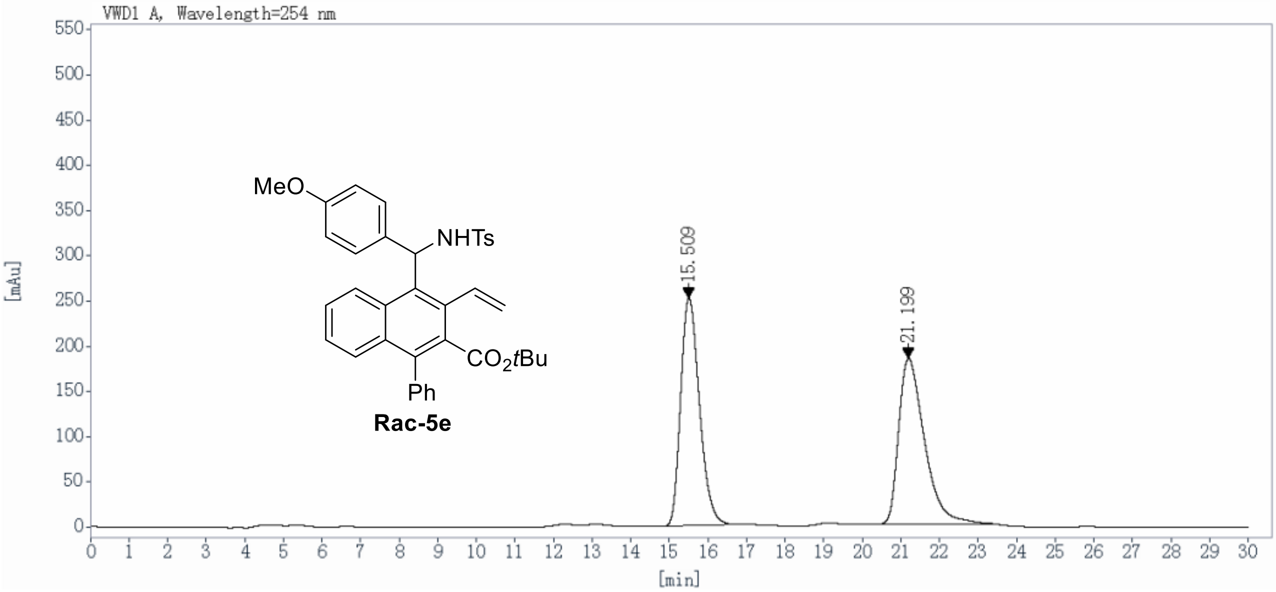
**5e**

$^1$H NMR (400 MHz, CDCl$_3$)

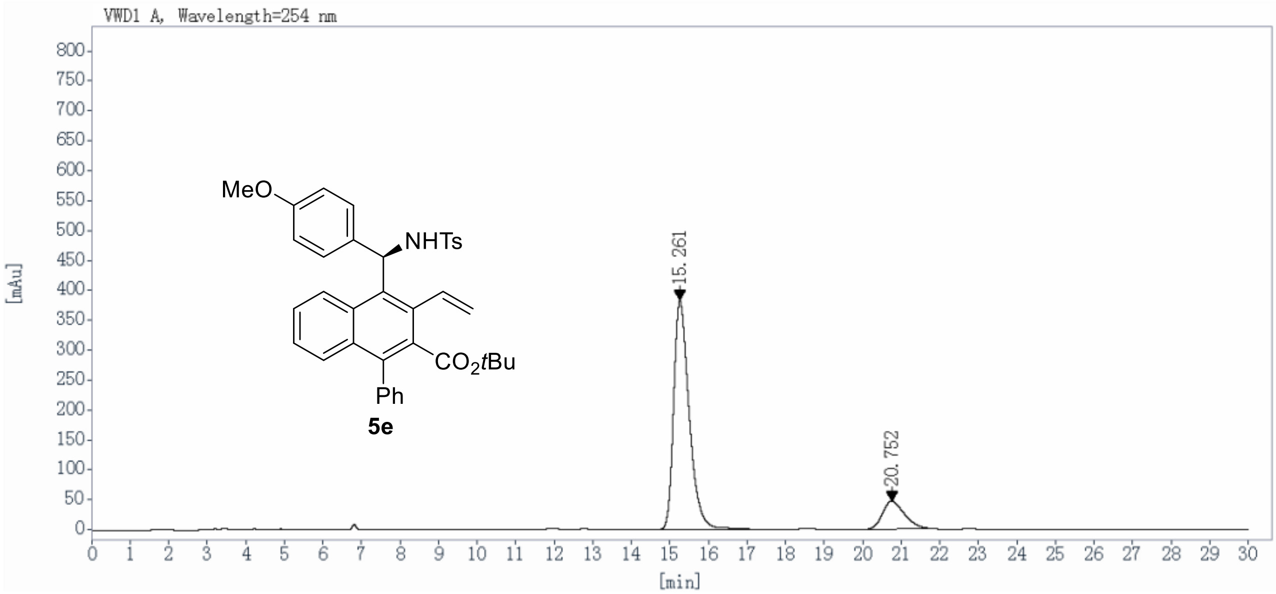


**5e**

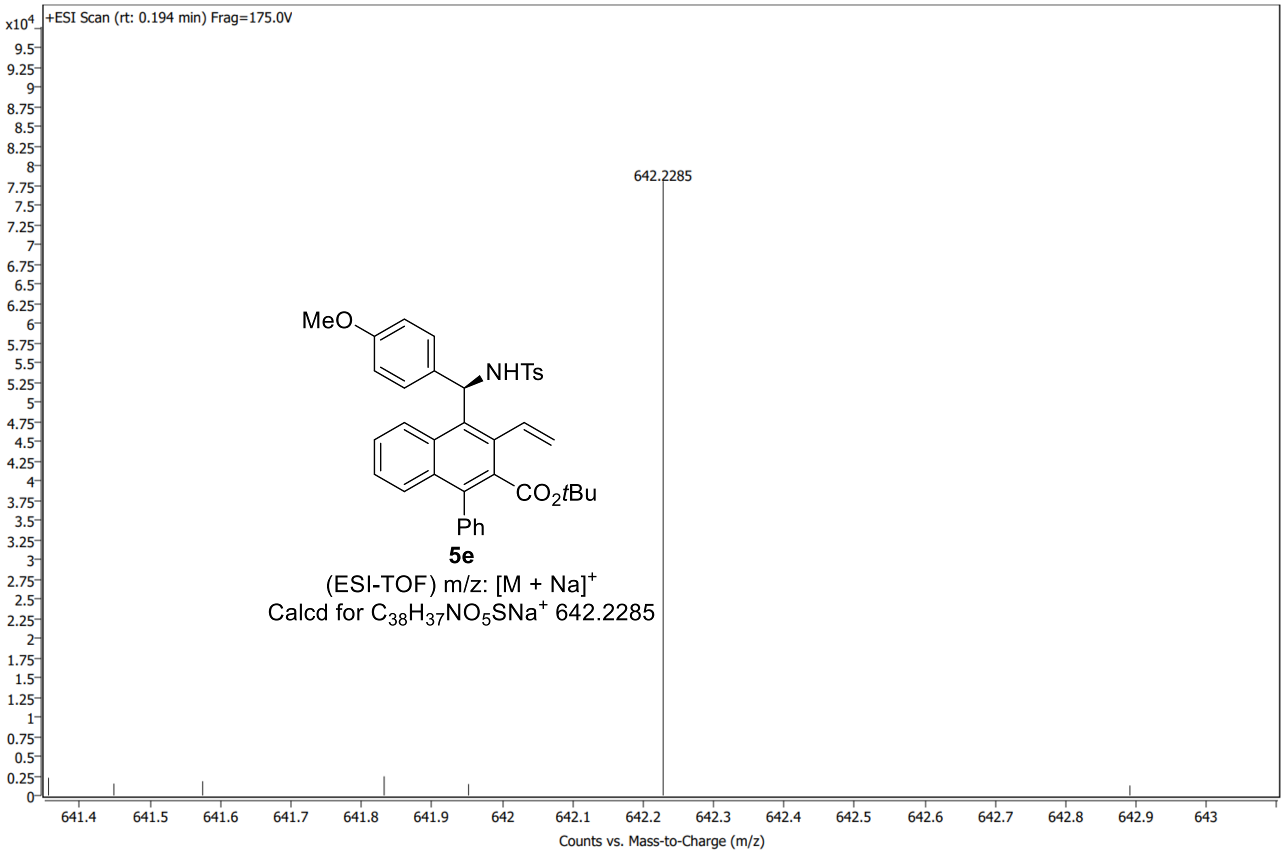
$^{13}$C NMR (150 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 15.509 | BB | 0.53 | 252.3438 | 8551.8818 | 50.1373 |
| 21.199 | BBA | 0.71 | 183.1120 | 8505.0342 | 49.8627 |
| | | | Totals: | 17056.9160 | 100.0000 |



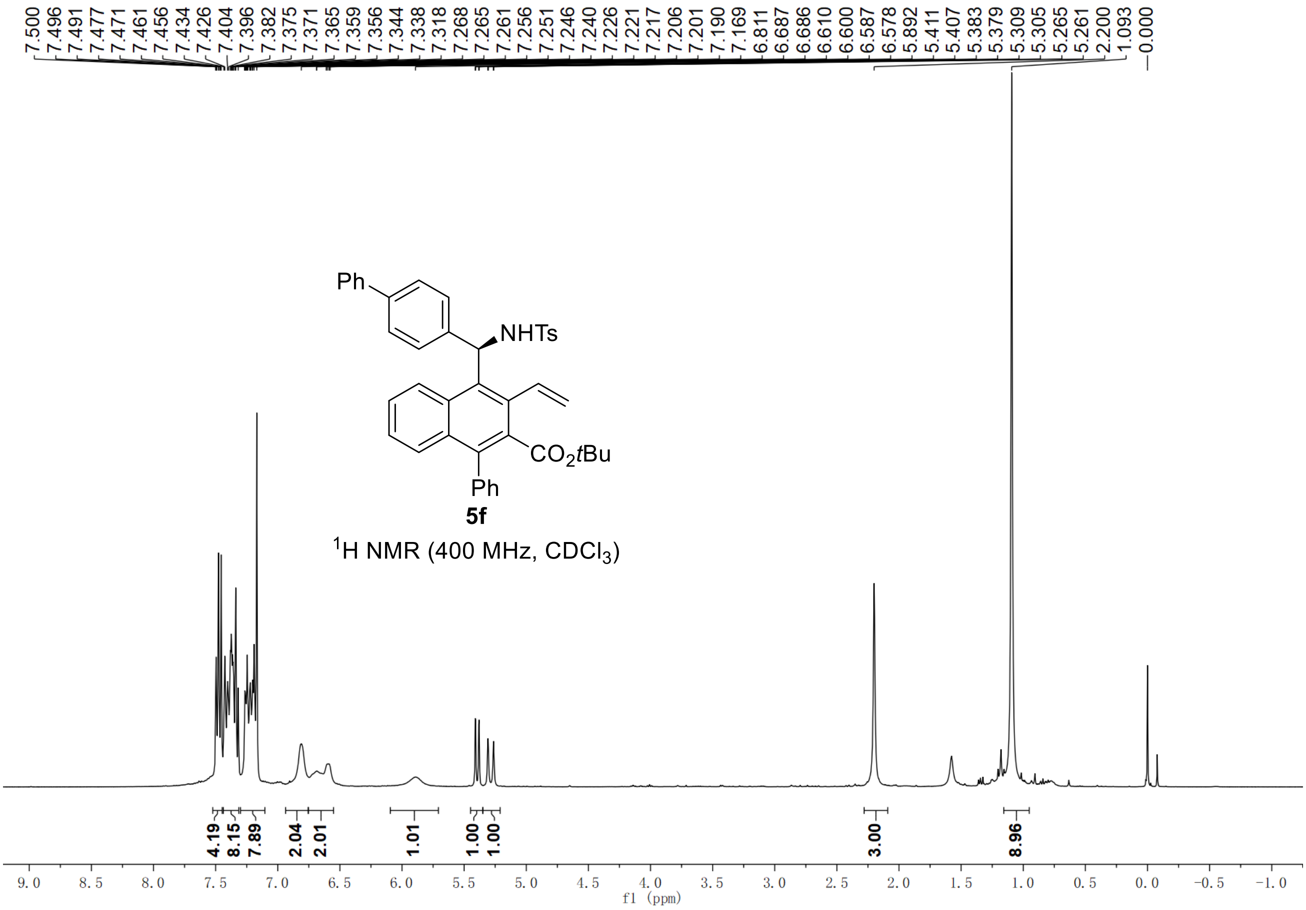
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 15.261 | BB | 0.43 | 382.7608 | 10767.6221 | 85.6492 |
| 20.752 | BBA | 0.61 | 45.9644 | 1804.1548 | 14.3508 |
| | | | Totals: | 12571.7769 | 100.0000 |

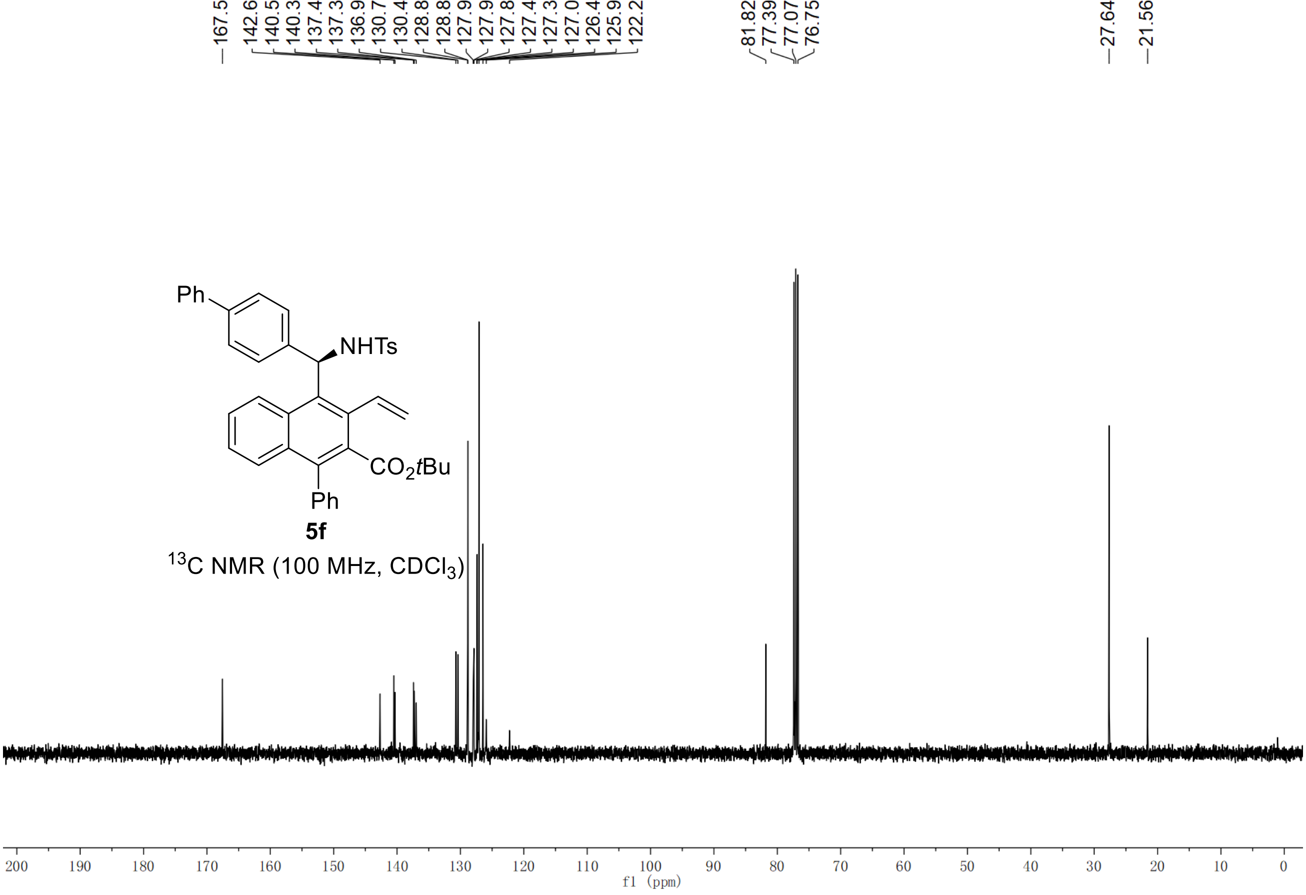


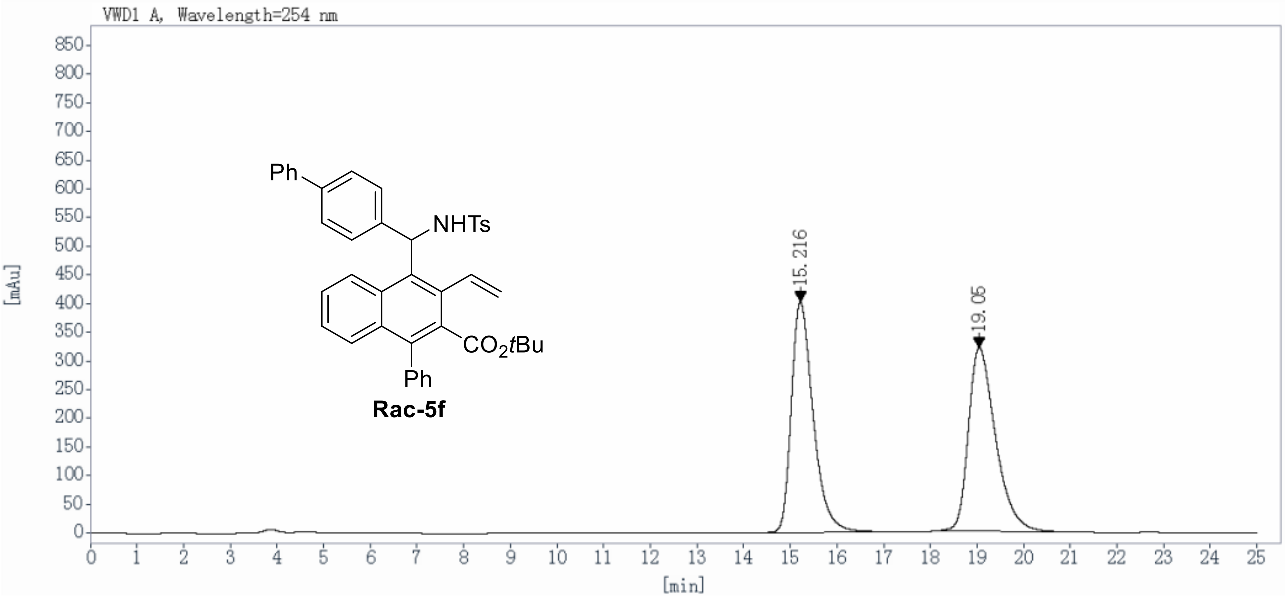
**5e**

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{38}H_{37}NO_5SNa^+$ 642.2285

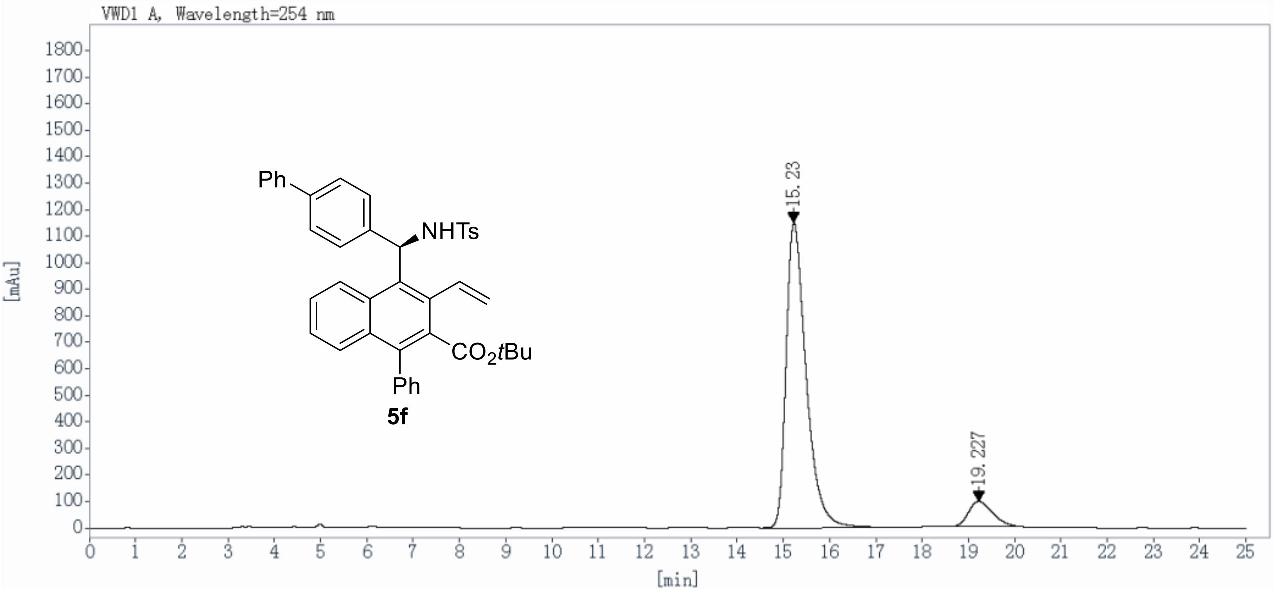

7.500
7.496
7.491
7.477
7.471
7.461
7.456
7.434
7.426
7.404
7.396
7.382
7.375
7.371
7.365
7.359
7.356
7.344
7.338
7.318
7.268
7.265
7.261
7.256
7.251
7.246
7.240
7.226
7.221
7.217
7.206
7.201
7.190
7.169
6.811
6.687
6.686
6.610
6.600
6.587
6.578
5.892
5.411
5.407
5.383
5.379
5.309
5.305
5.265
5.261
2.200
1.093
0.000
Ph
NHTs
CO2tBu
Ph
5f
1H NMR (400 MHz, CDCl3)
4.19
8.15
7.89
2.04
2.01
1.01
1.00
1.00
3.00
8.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


167.54
142.68
140.50
140.32
137.41
137.30
136.97
130.73
130.40
128.86
128.82
127.99
127.93
127.86
127.42
127.36
127.07
126.45
125.93
122.24
81.82
77.39
77.07
76.75
27.64
21.56
Ph
NHTs
CO2tBu
Ph
5f
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



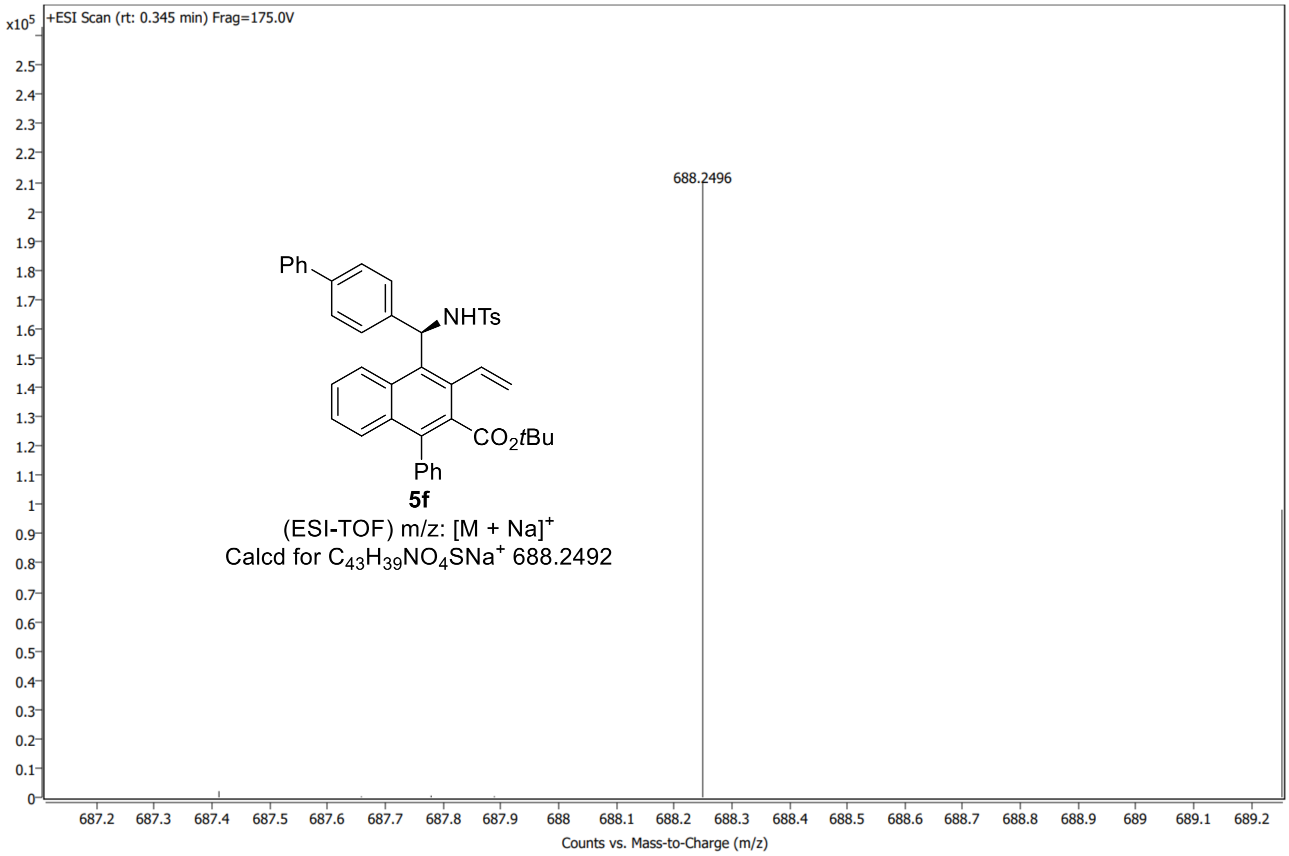
**Rac-5f**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 15.216 | BB | 0.50 | 401.9093 | 13107.0479 | 50.5471 |
| 19.050 | BB | 0.59 | 318.9063 | 12823.3057 | 49.4529 |
| | | | Totals: | 25930.3535 | 100.0000 |



**5f**

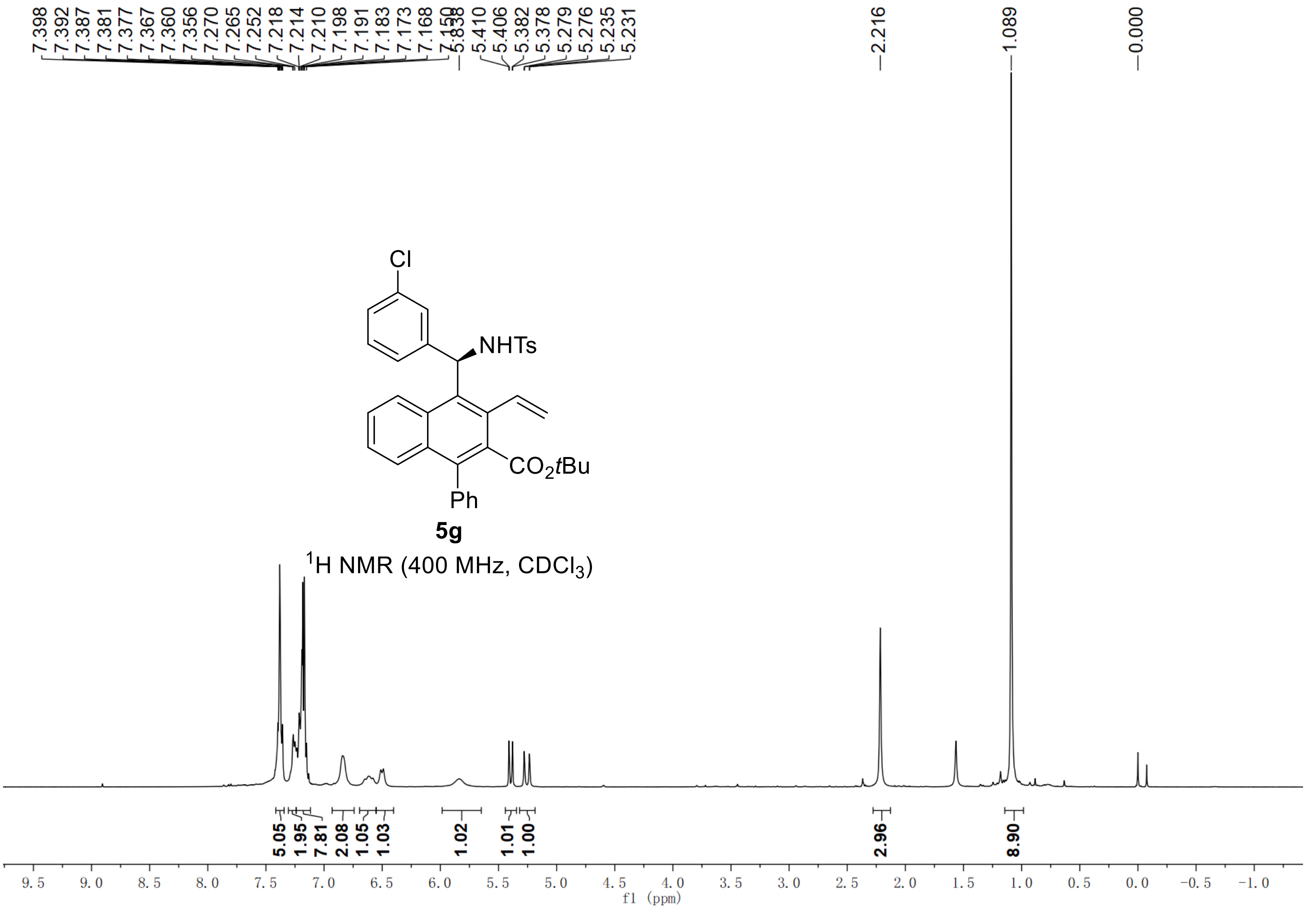
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 15.230 | BBA | 0.45 | 1150.4845 | 34432.0898 | 90.7963 |
| 19.227 | BBA | 0.56 | 95.6247 | 3490.2544 | 9.2037 |
| | | | Totals: | 37922.3442 | 100.0000 |

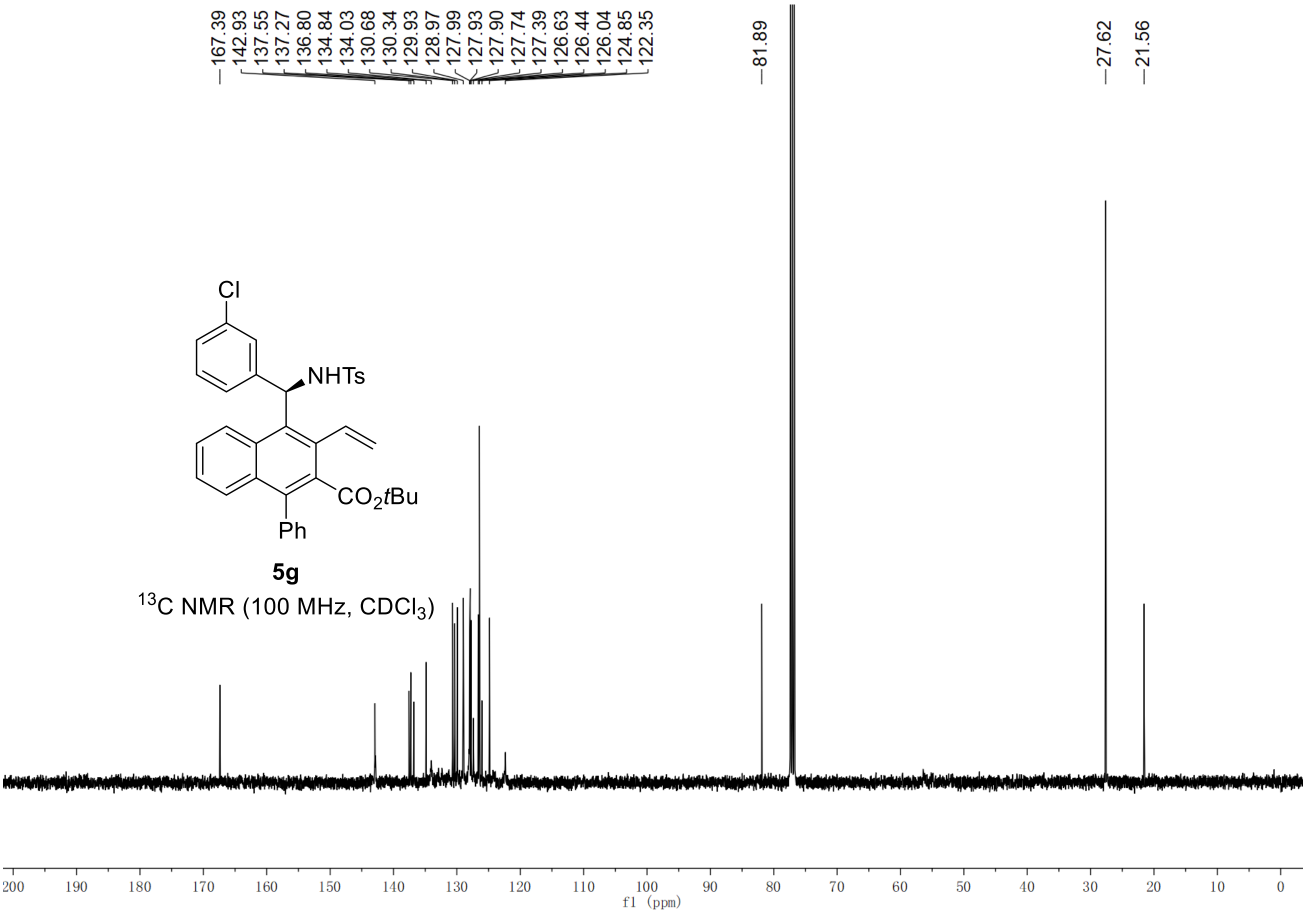


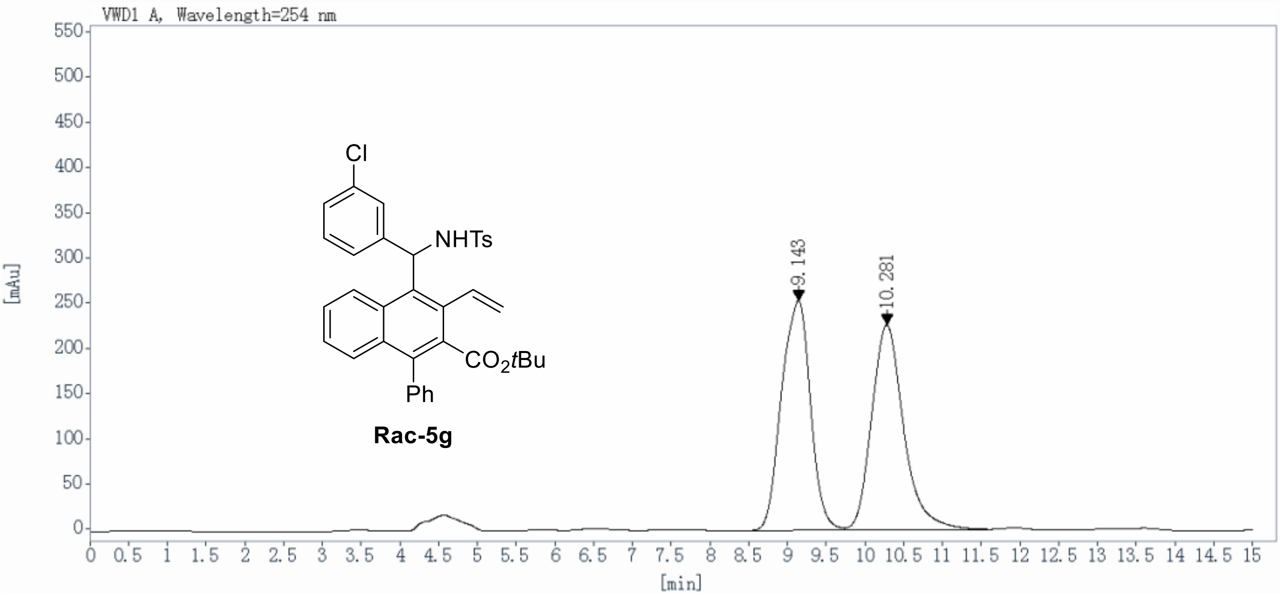
**5f**

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{43}H_{39}NO_4SNa^+$ 688.2492

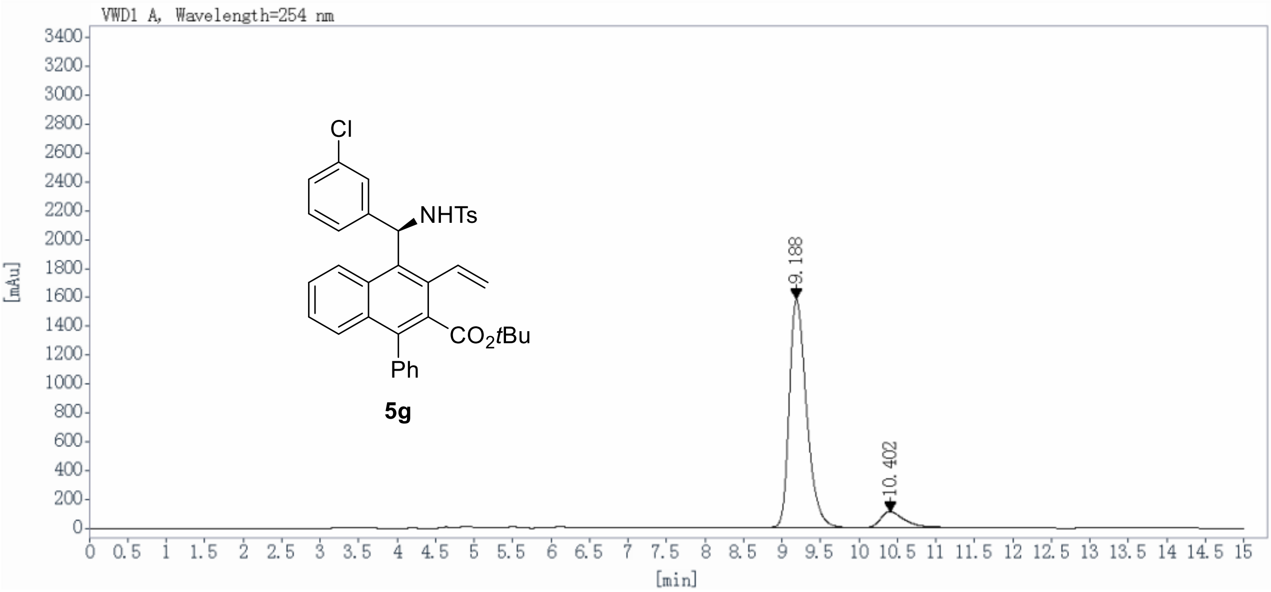

7.398
7.392
7.387
7.381
7.377
7.367
7.360
7.356
7.270
7.265
7.252
7.218
7.214
7.210
7.198
7.191
7.183
7.173
7.168
7.150
5.838
5.410
5.406
5.382
5.378
5.279
5.276
5.235
5.231
2.216
1.089
0.000
Cl
NHTs
CO2tBu
Ph
5g
1H NMR (400 MHz, CDCl3)
5.05
1.95
7.81
2.08
1.05
1.03
1.02
1.01
1.00
2.96
8.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.39
142.93
137.55
137.27
136.80
134.84
134.03
130.68
130.34
129.93
128.97
127.99
127.93
127.90
127.74
127.39
126.63
126.44
126.04
124.85
122.35
81.89
27.62
21.56
Cl
NHTs
CO2tBu
Ph
5g
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



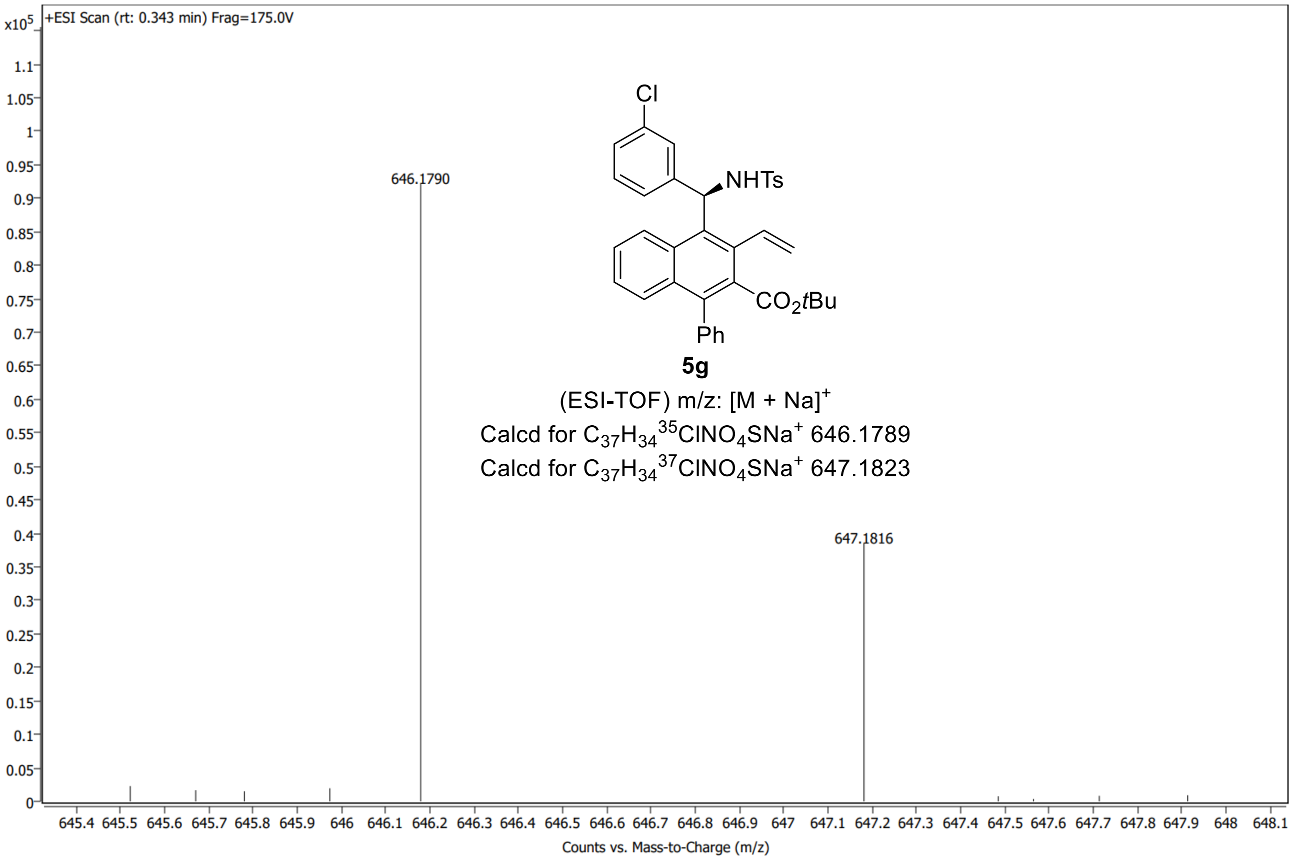
**Rac-5g**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.143 | BV | 0.42 | 253.9170 | 6602.9429 | 50.3202 |
| 10.281 | VB | 0.44 | 226.8676 | 6518.9121 | 49.6798 |
|  |  |  | Totals: | 13121.8550 | 100.0000 |



**5g**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.188 | BB | 0.24 | 1583.1528 | 24892.0000 | 91.5290 |
| 10.402 | BBA | 0.32 | 109.6029 | 2303.7468 | 8.4710 |
|  |  |  | Totals: | 27195.7468 | 100.0000 |

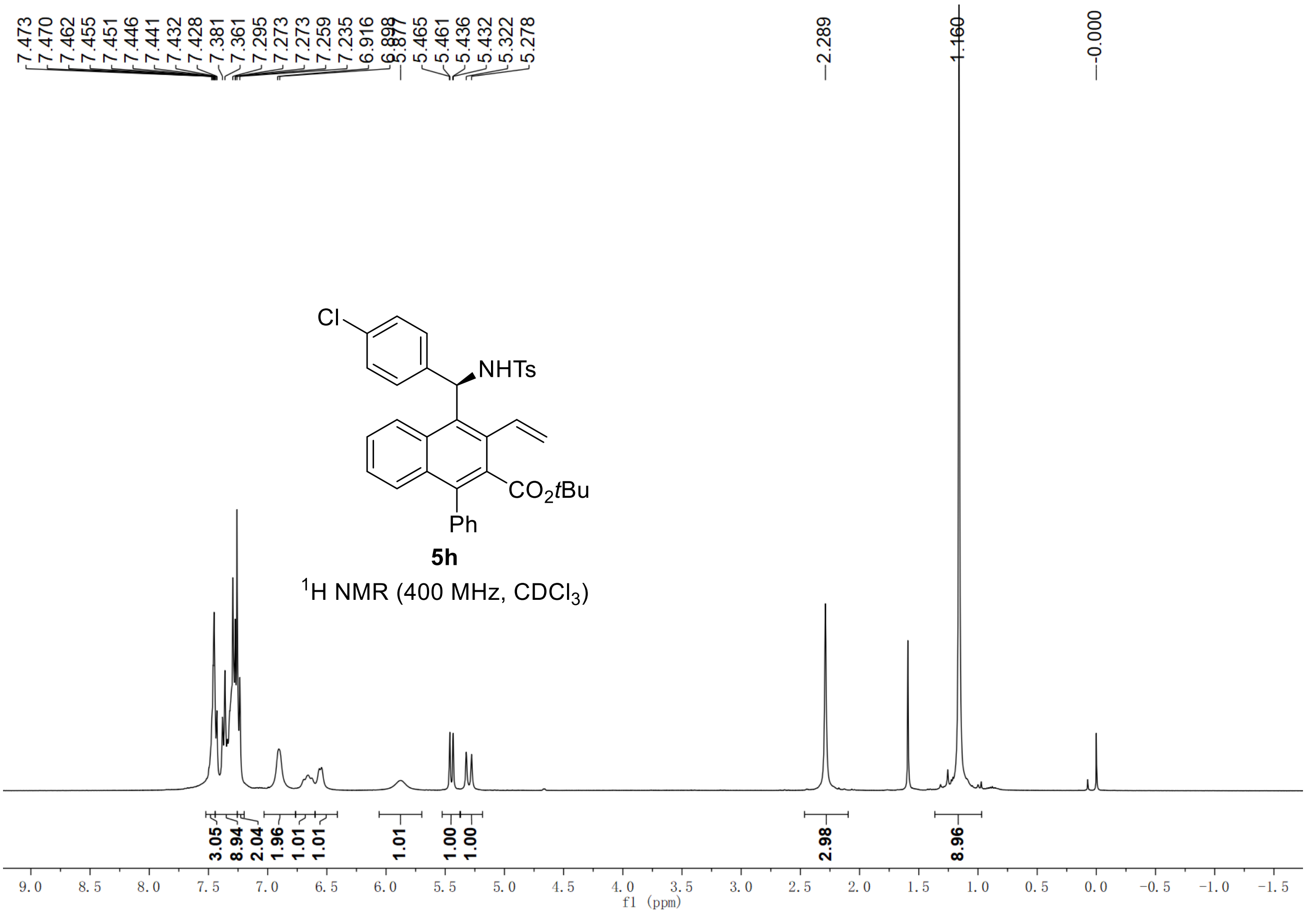


**5g**

(ESI-TOF) m/z: $[M + Na]^+$

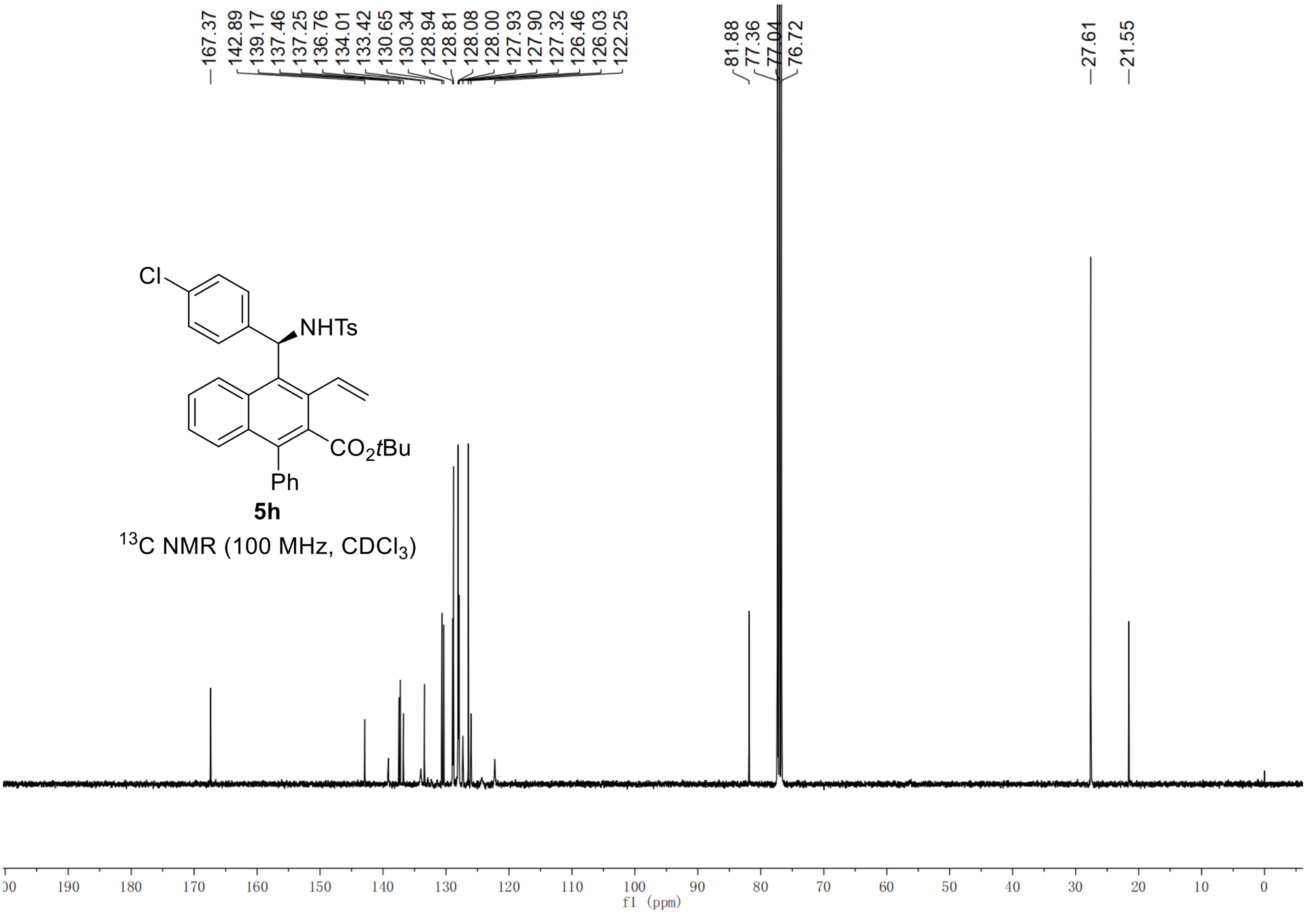
Calcd for $C_{37}H_{34}{}^{35}ClNO_4SNa^+$ 646.1789

Calcd for $C_{37}H_{34}{}^{37}ClNO_4SNa^+$ 647.1823



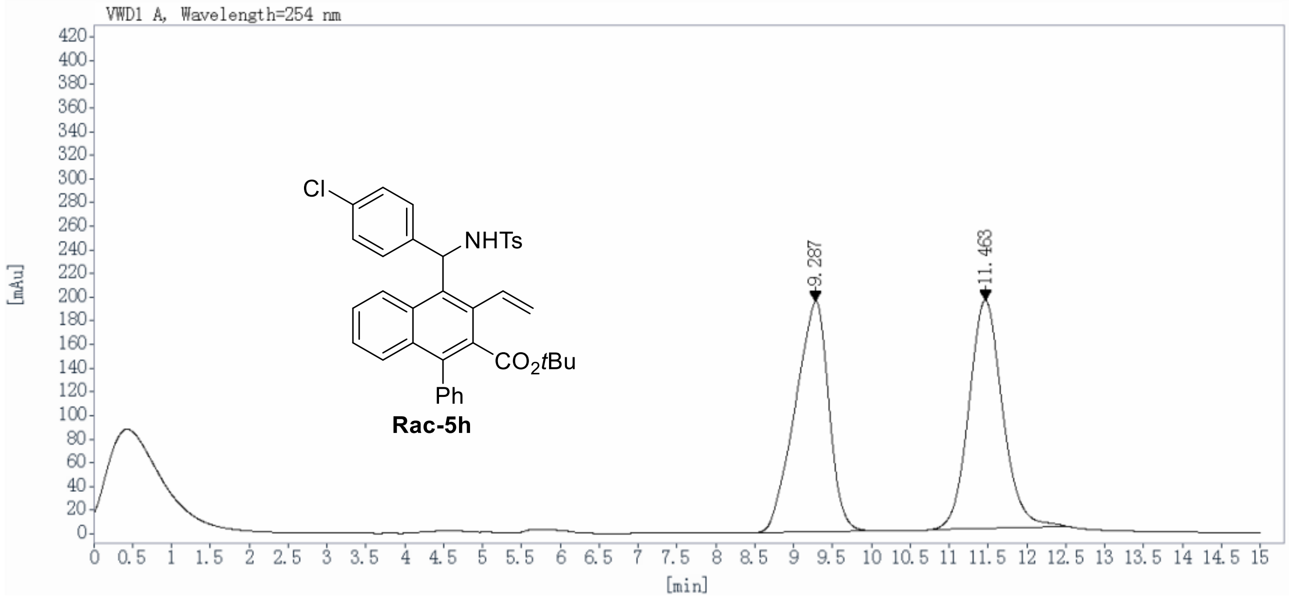
**5h**

$^1$H NMR (400 MHz, $CDCl_3$)

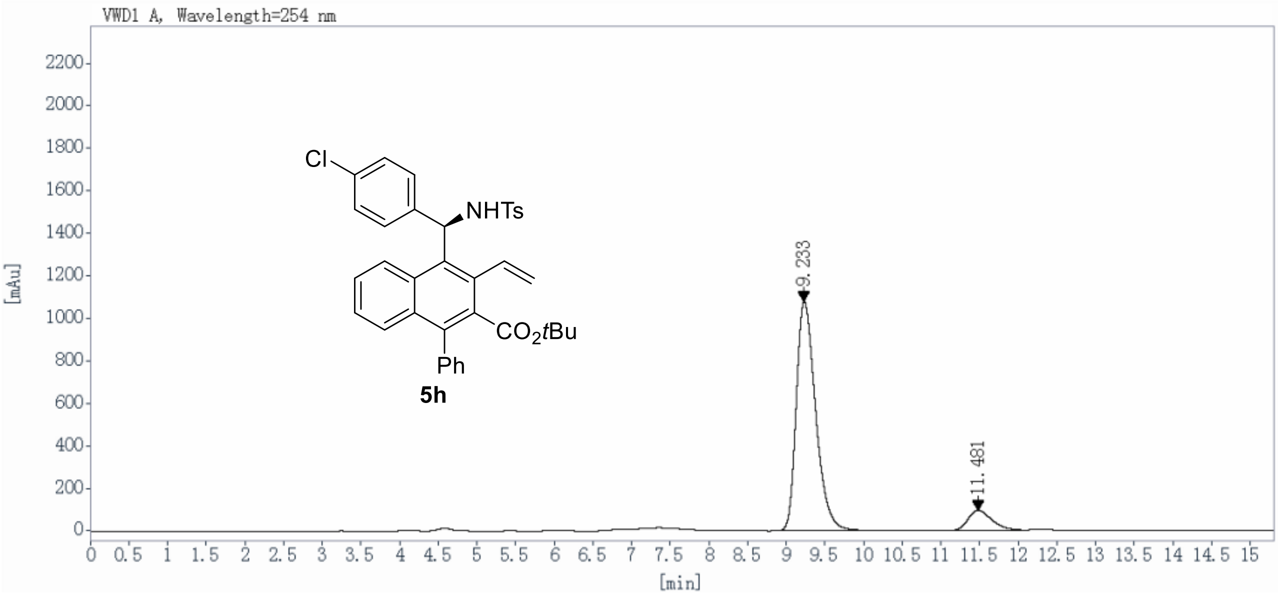


**5h**

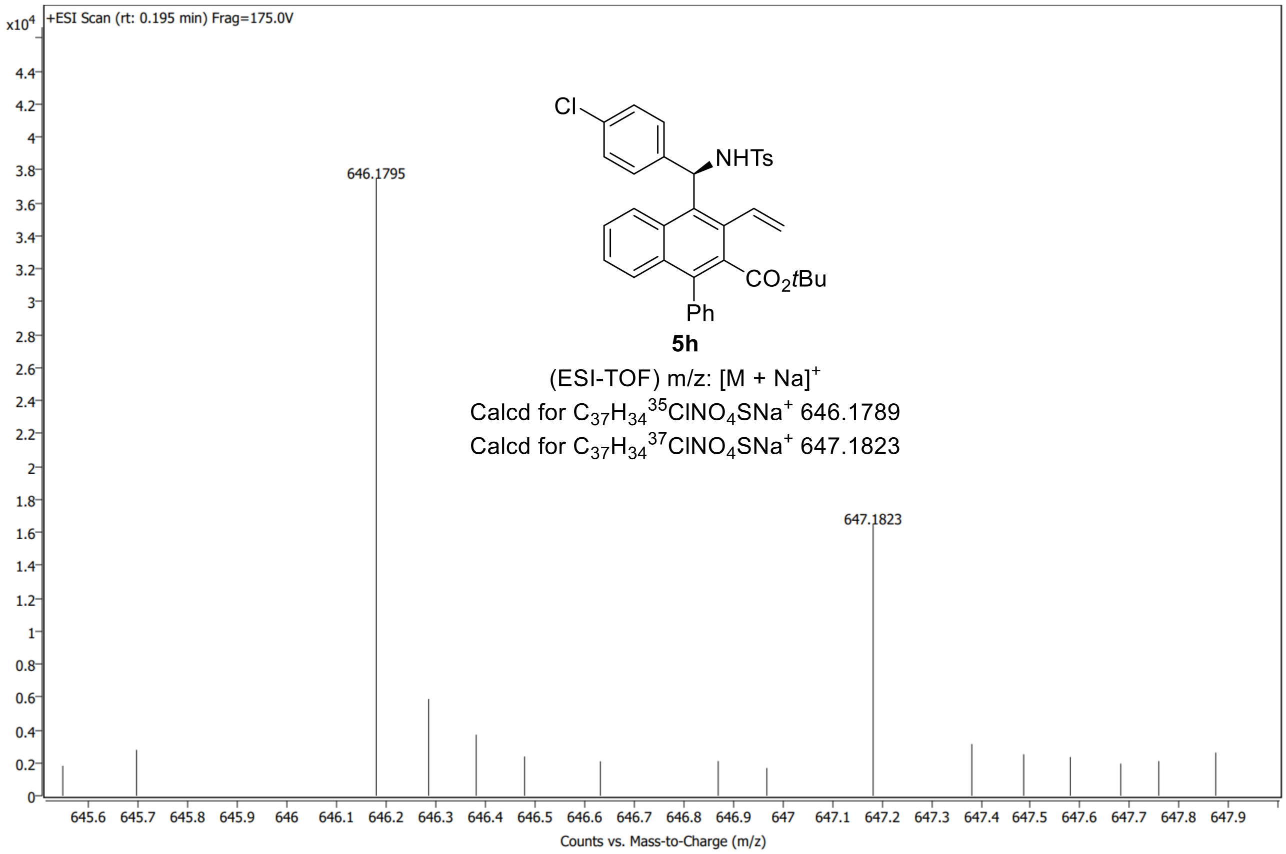
$^{13}$C NMR (100 MHz, $CDCl_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.287 | BB | 0.48 | 194.7628 | 5861.9072 | 50.2757 |
| 11.463 | BBA | 0.46 | 193.0011 | 5797.6216 | 49.7243 |
|  |  |  | Totals: | 11659.5288 | 100.0000 |



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.233 | BB | 0.27 | 1079.9955 | 18781.6973 | 90.2885 |
| 11.481 | BB | 0.33 | 94.1222 | 2020.1724 | 9.7115 |
|  |  |  | Totals: | 20801.8696 | 100.0000 |

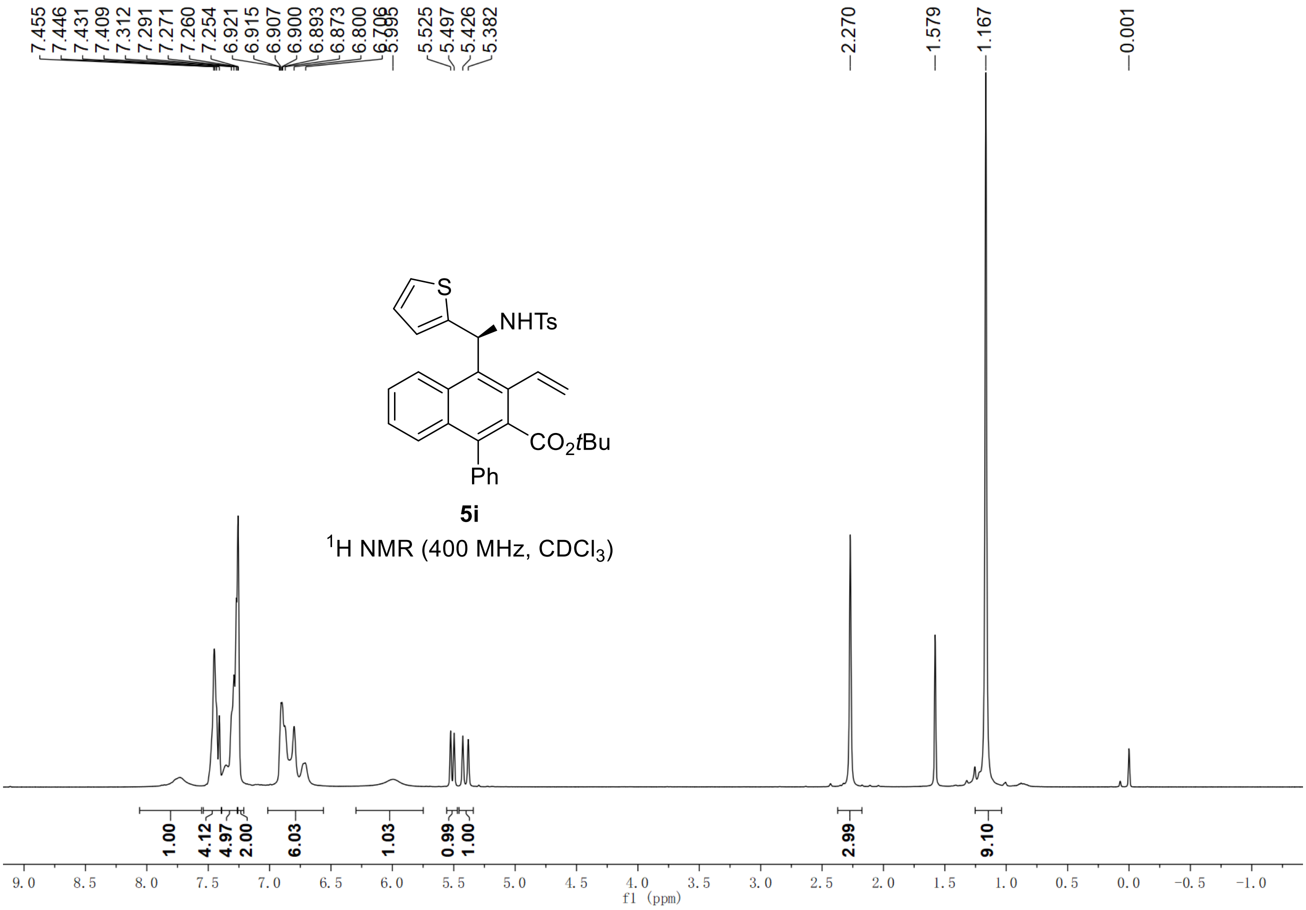


**5h**

(ESI-TOF) m/z: $[M + Na]^+$

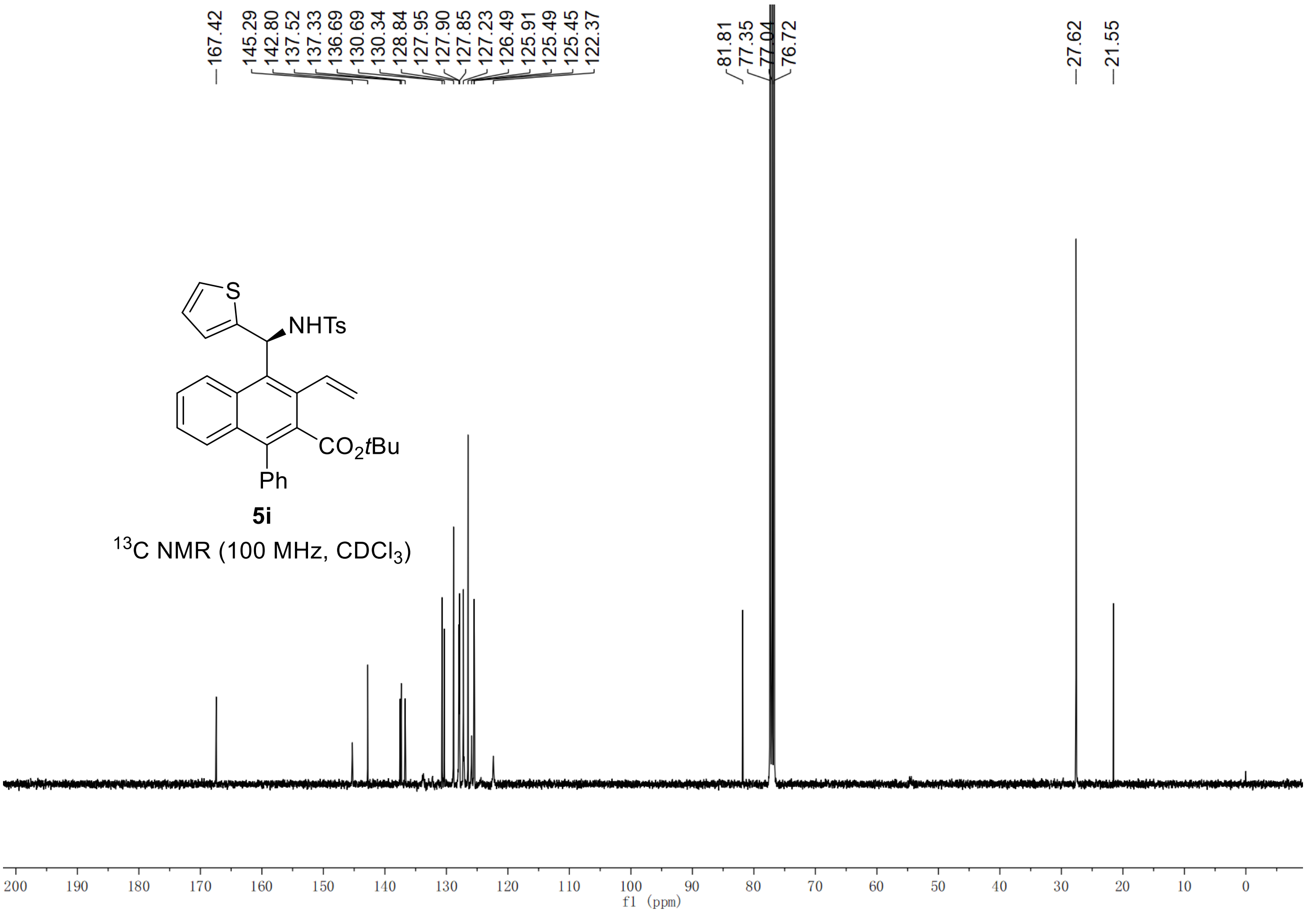
Calcd for $C_{37}H_{34}{}^{35}ClNO_4SNa^+$ 646.1789

Calcd for $C_{37}H_{34}{}^{37}ClNO_4SNa^+$ 647.1823



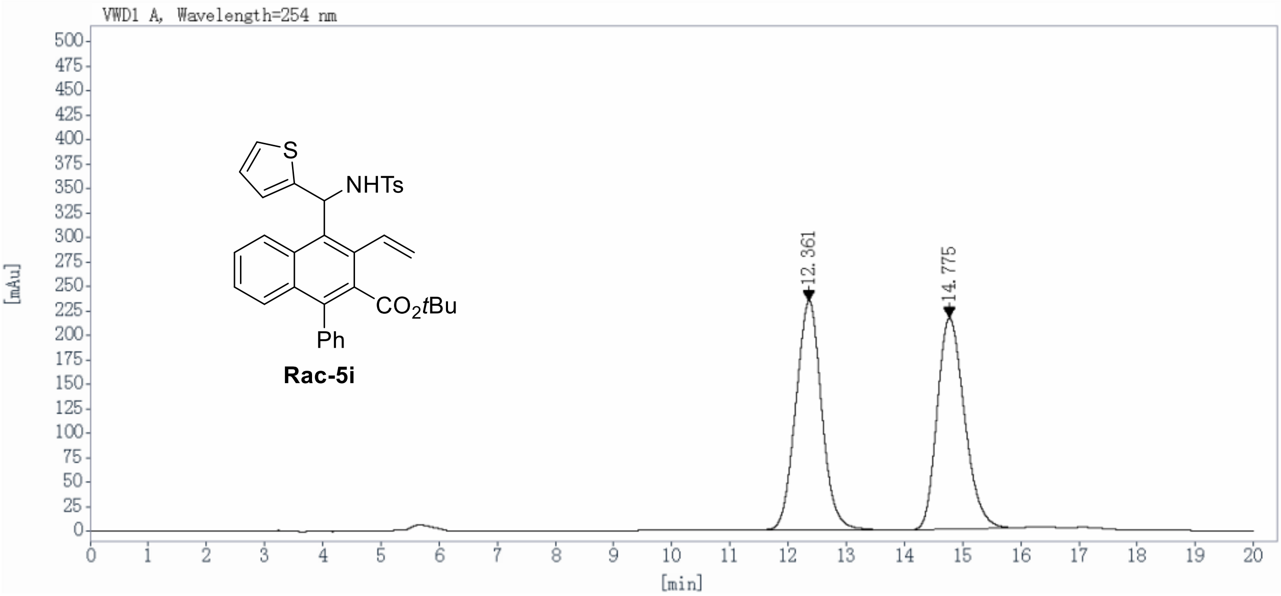
**5i**

$^1$H NMR (400 MHz, CDCl$_3$)

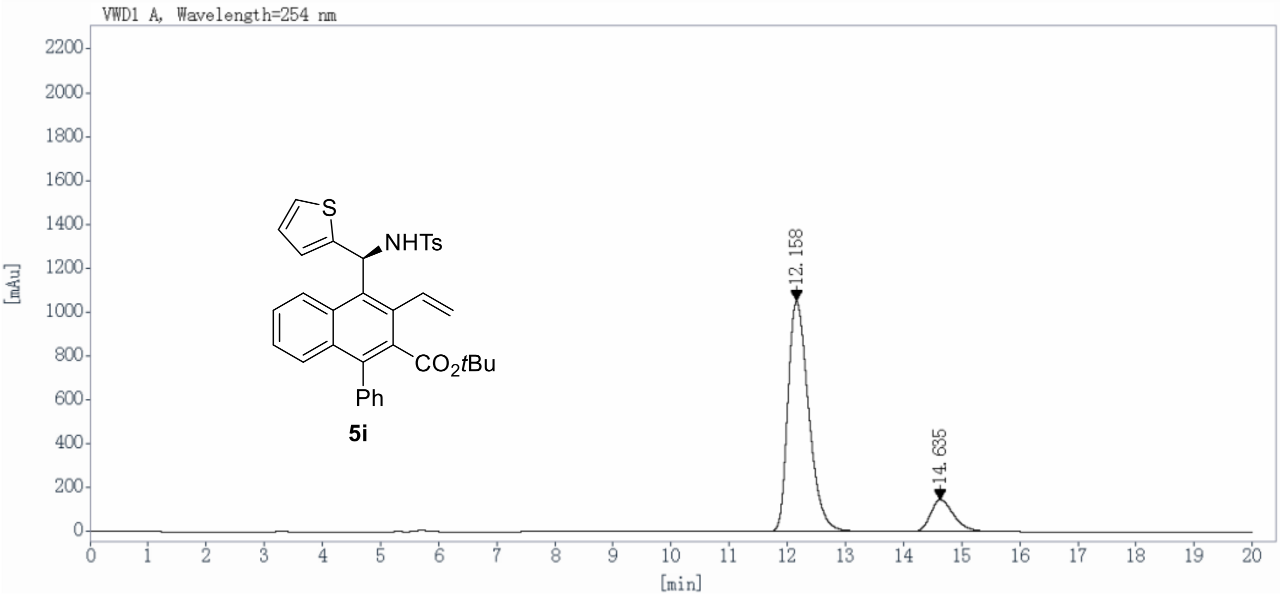


**5i**

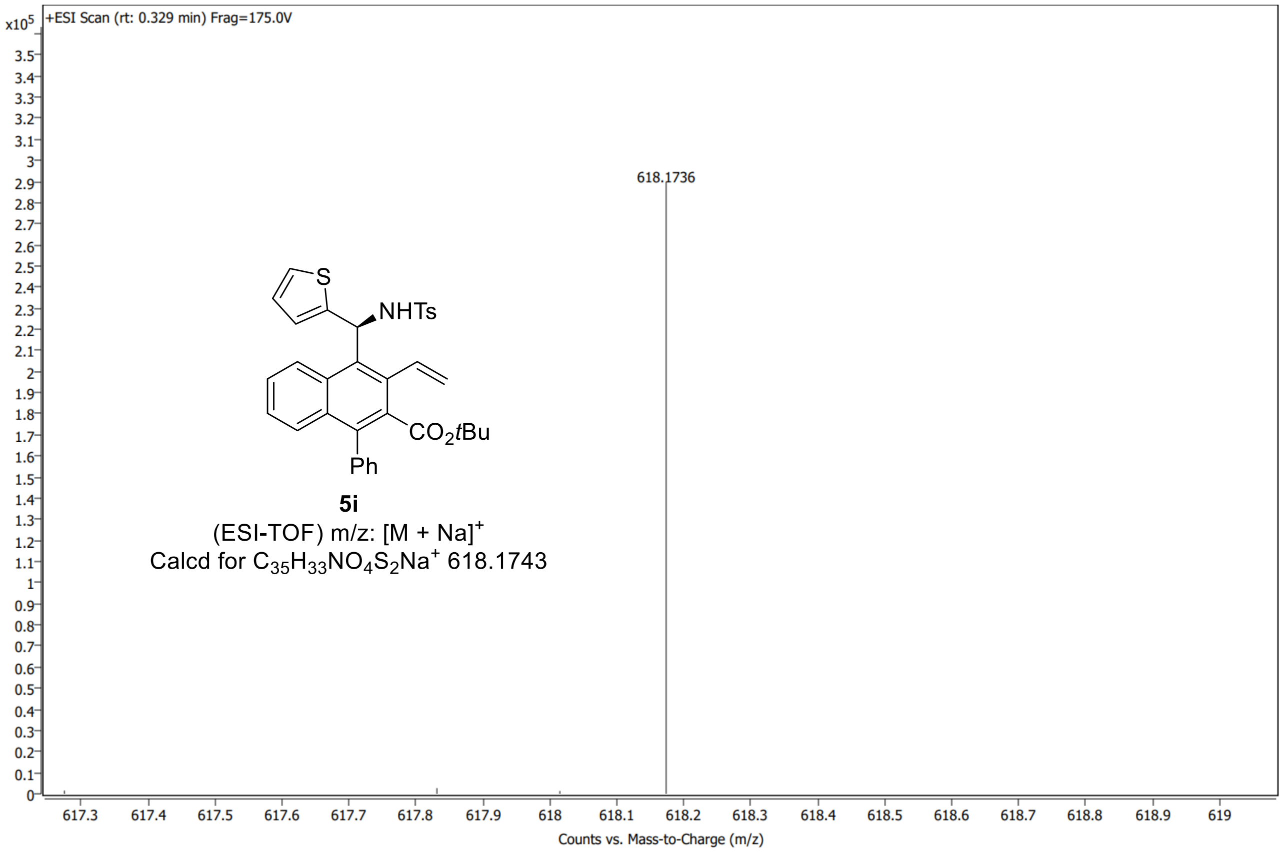
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 12.361 | BBA | 0.48 | 234.1625 | 7225.2637 | 50.5206 |
| 14.775 | BB | 0.51 | 216.1072 | 7076.3452 | 49.4794 |
| | | | Totals: | 14301.6089 | 100.0000 |



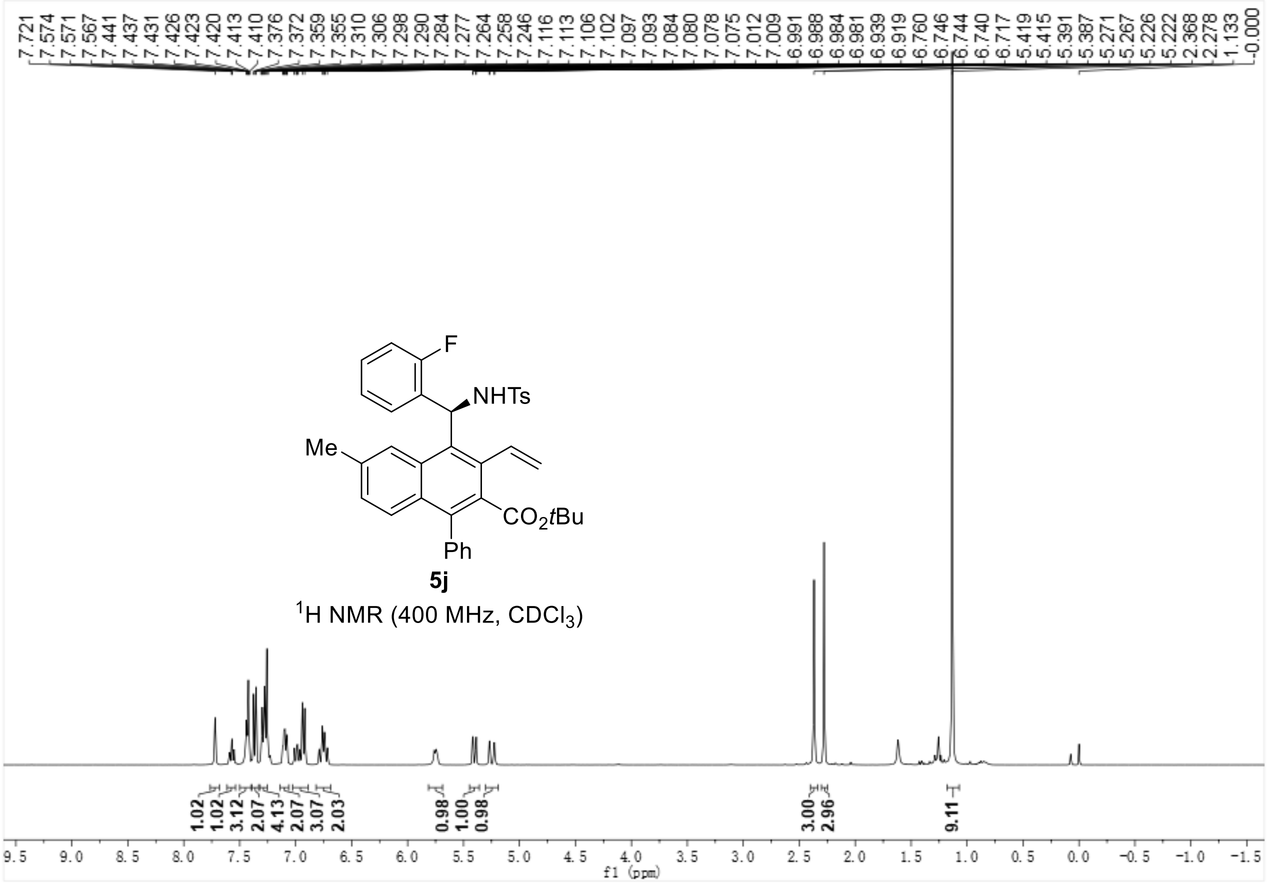
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 12.158 | BBA | 0.39 | 1049.2786 | 25989.9453 | 86.6007 |
| 14.635 | BBA | 0.43 | 144.7619 | 4021.2808 | 13.3993 |
| | | | Totals: | 30011.2261 | 100.0000 |



**5i**

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{35}H_{33}NO_4S_2Na^+$ 618.1743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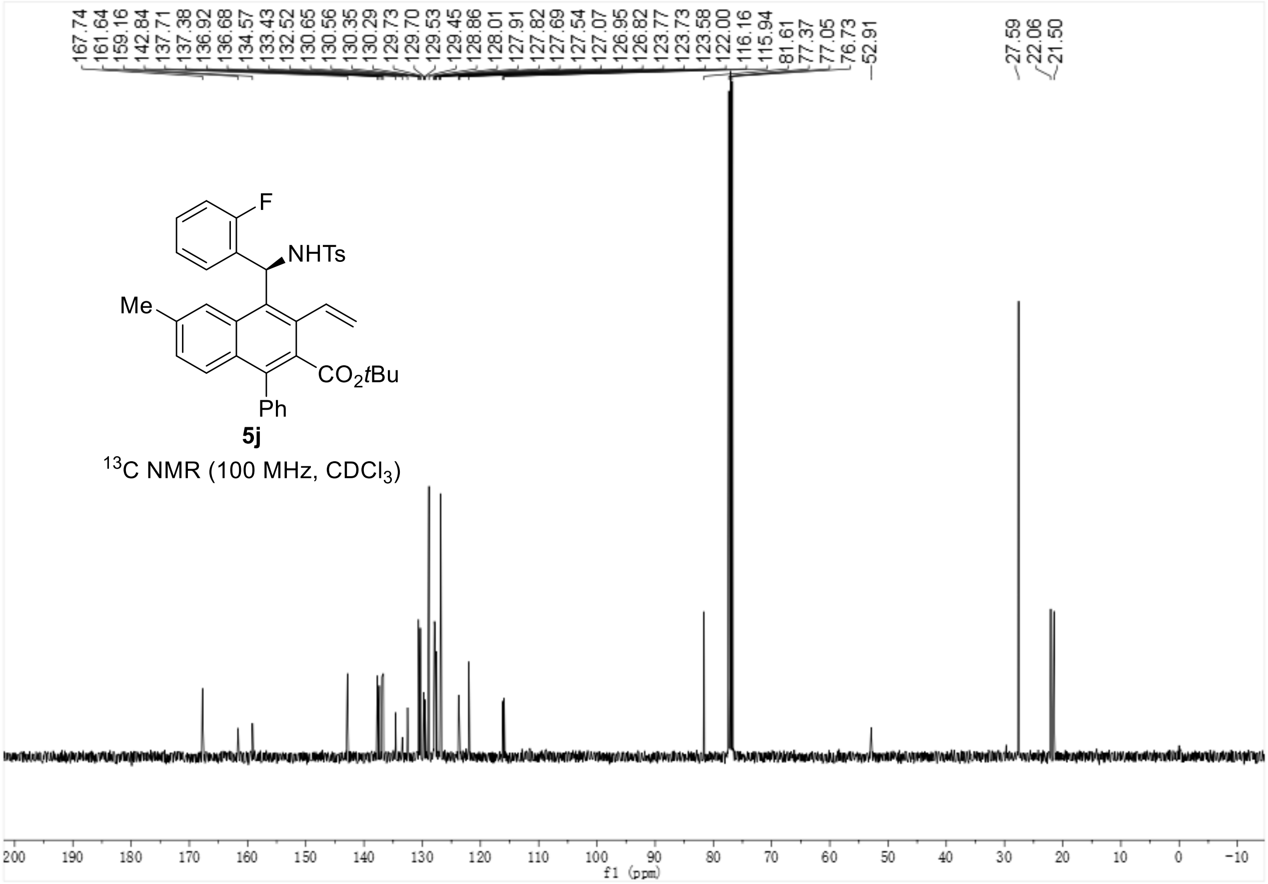
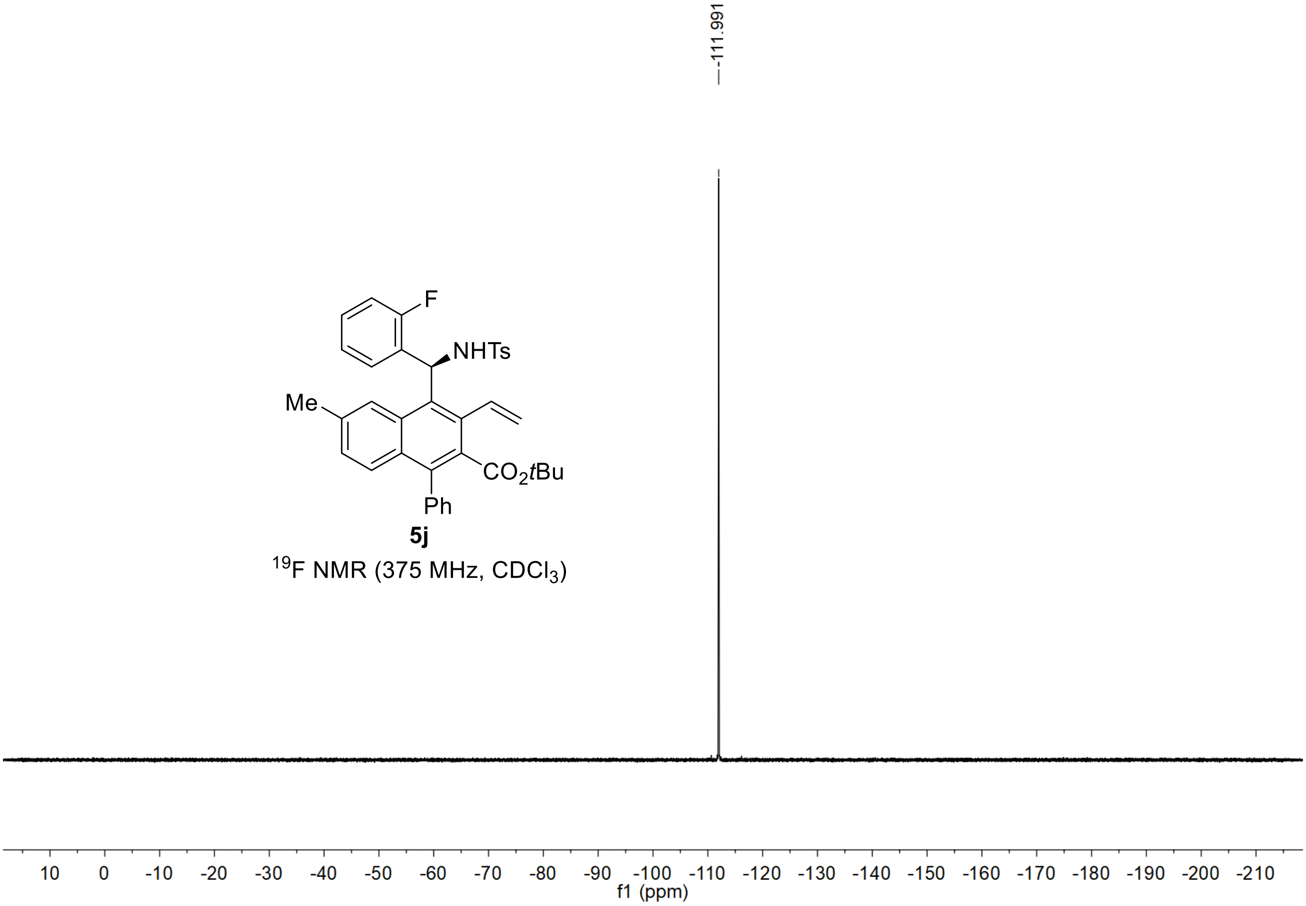
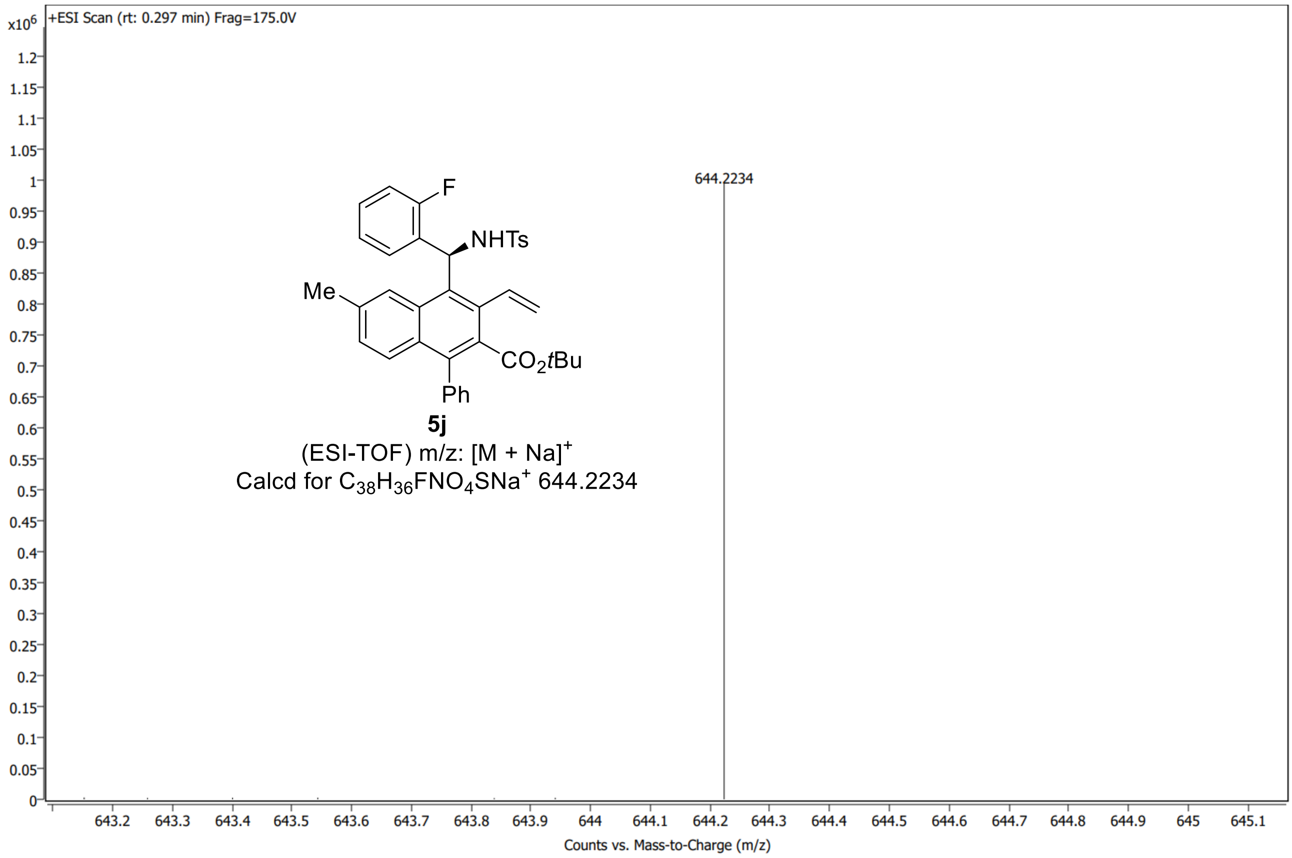
7.574
7.571
7.567
7.441
7.437
7.431
7.426
7.423
7.420
7.413
7.410
7.376
7.372
7.359
7.355
7.310
7.306
7.298
7.290
7.284
7.277
7.264
7.258
7.246
7.116
7.113
7.106
7.102
7.097
7.093
7.084
7.080
7.078
7.075
7.012
7.009
6.991
6.988
6.984
6.981
6.939
6.919
6.760
6.746
6.744
6.740
6.717
5.419
5.415
5.391
5.387
5.271
5.267
5.226
5.222
2.368
2.278
1.133
-0.000
F
NHTs
Me
CO2tBu
Ph
5j
1H NMR (400 MHz, CDCl3)
1.02
1.02
3.12
2.07
4.13
2.07
3.07
2.03
0.98
1.00
0.98
3.00
2.96
9.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


167.74
161.64
159.16
142.84
137.71
137.38
136.92
136.68
134.57
133.43
132.52
130.65
130.56
130.35
130.29
129.73
129.70
129.53
129.45
128.86
128.01
127.91
127.82
127.69
127.54
127.07
126.95
126.82
123.77
123.73
123.58
122.00
116.16
115.94
81.61
77.37
77.05
76.73
52.91
27.59
22.06
21.50
F
NHTs
Me
CO2tBu
Ph
5j
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



**5j**

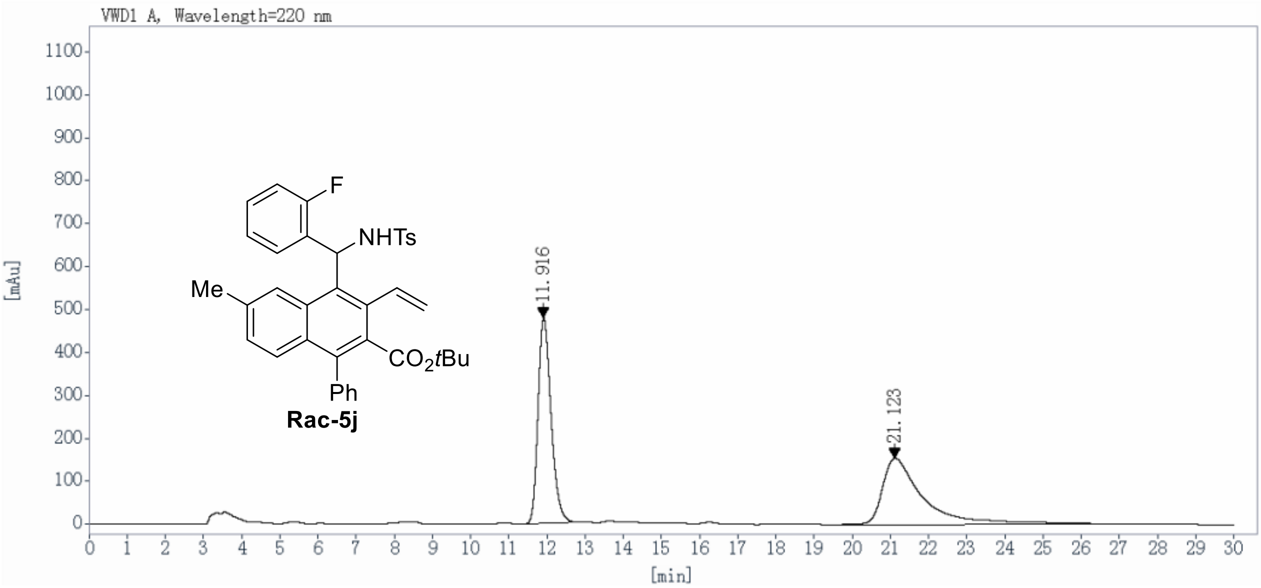
$^{19}$F NMR (375 MHz, CDCl$_3$)



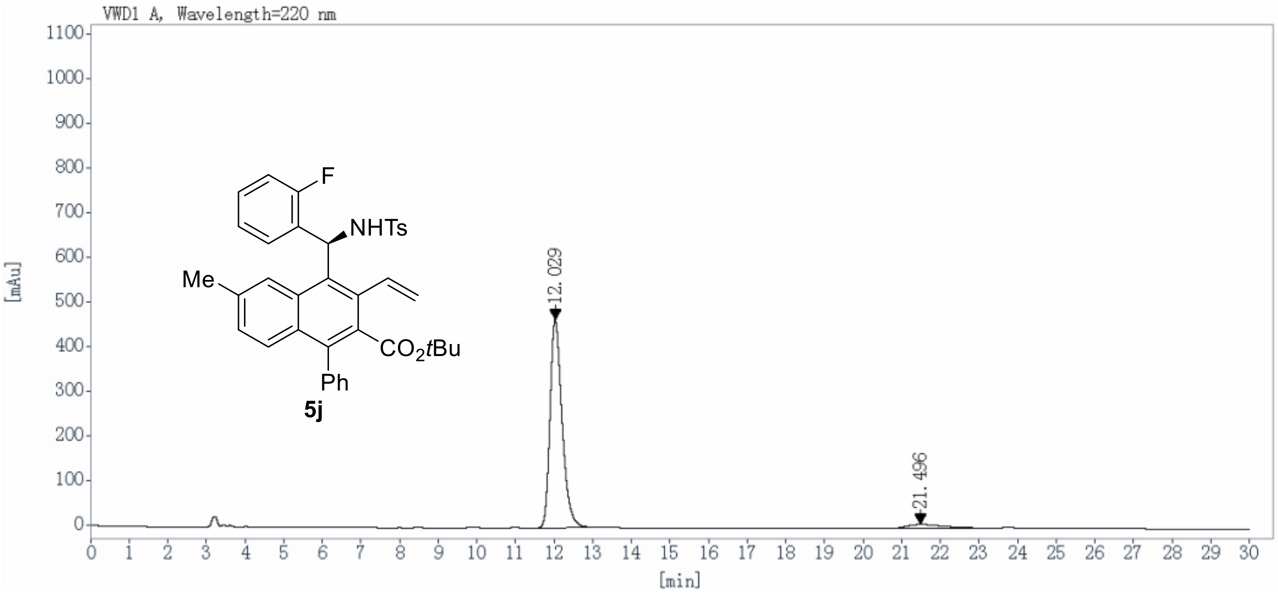
**5j**

(ESI-TOF) m/z: [M + Na]$^+$

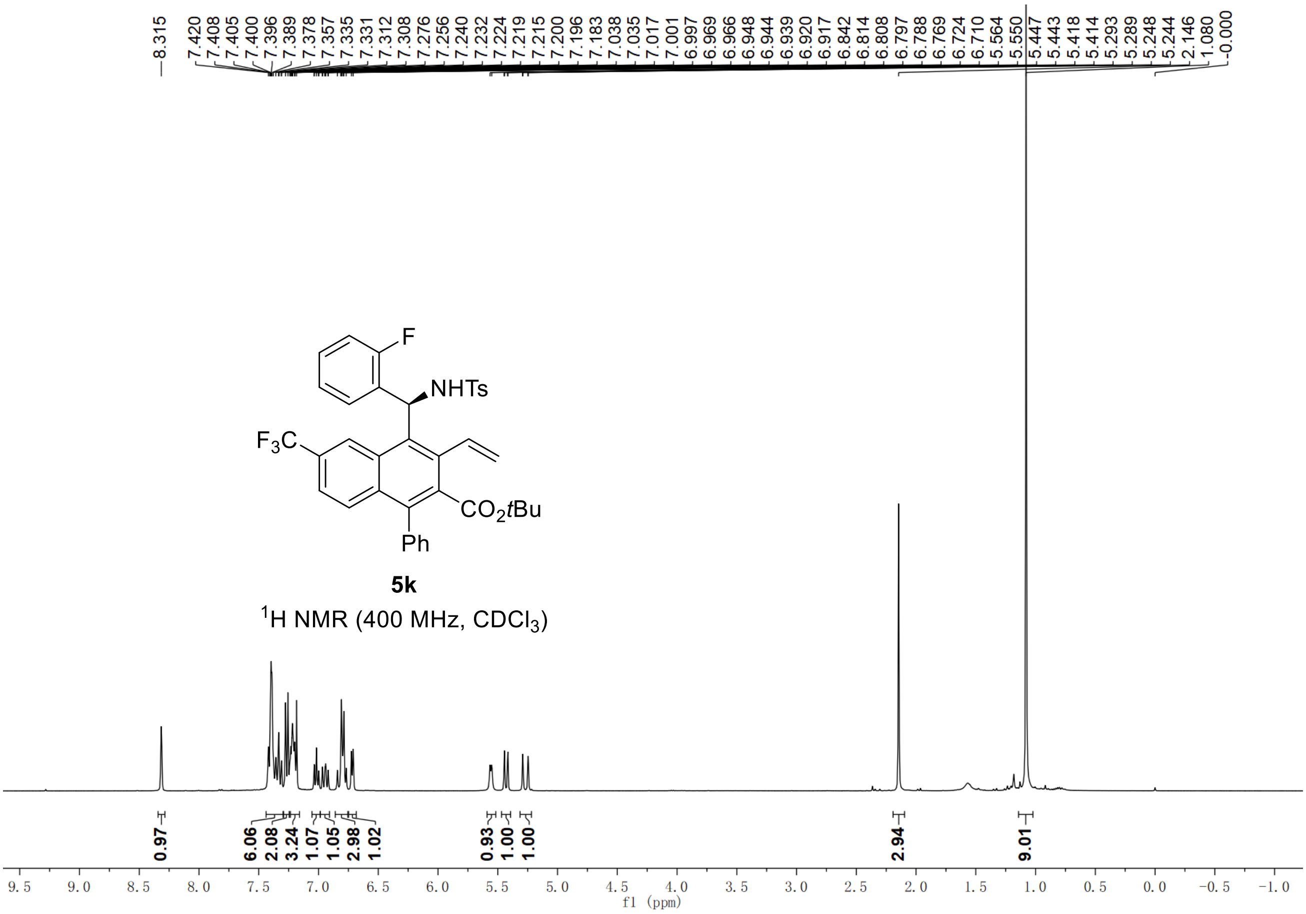
Calcd for $C_{38}H_{36}FNO_4SNa^+$ 644.2234



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 11.916 | BV R | 0.36 | 478.4497 | 11309.1582 | 50.3392 |
| 21.123 | BBA | 1.04 | 153.6520 | 11156.7617 | 49.6608 |
| | | | Totals: | 22465.9199 | 100.0000 |

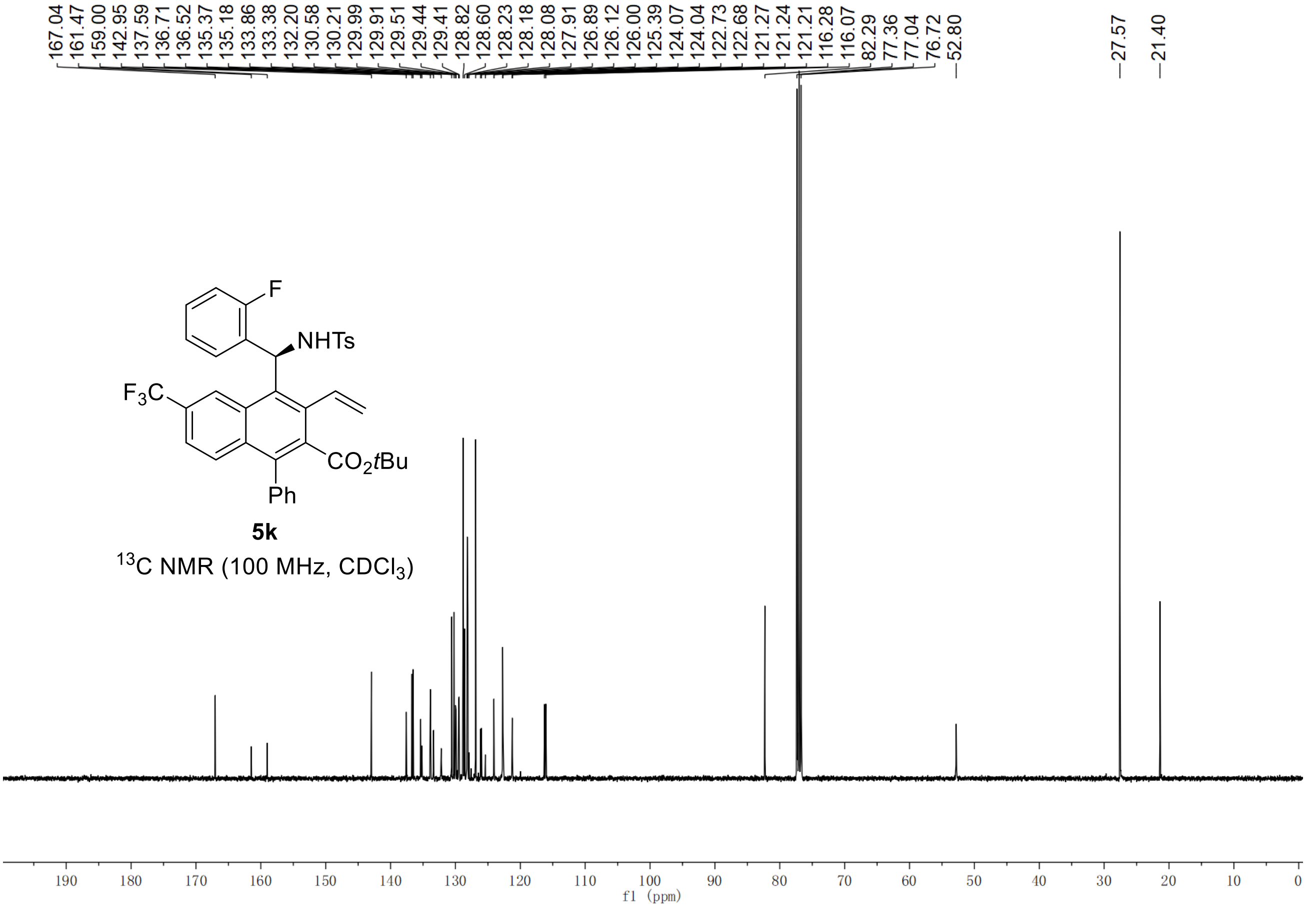


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 12.029 | BBA | 0.33 | 466.0885 | 10085.8760 | 94.4656 |
| 21.496 | BB | 0.97 | 8.8415 | 590.9008 | 5.5344 |
| | | | Totals: | 10676.7767 | 100.0000 |



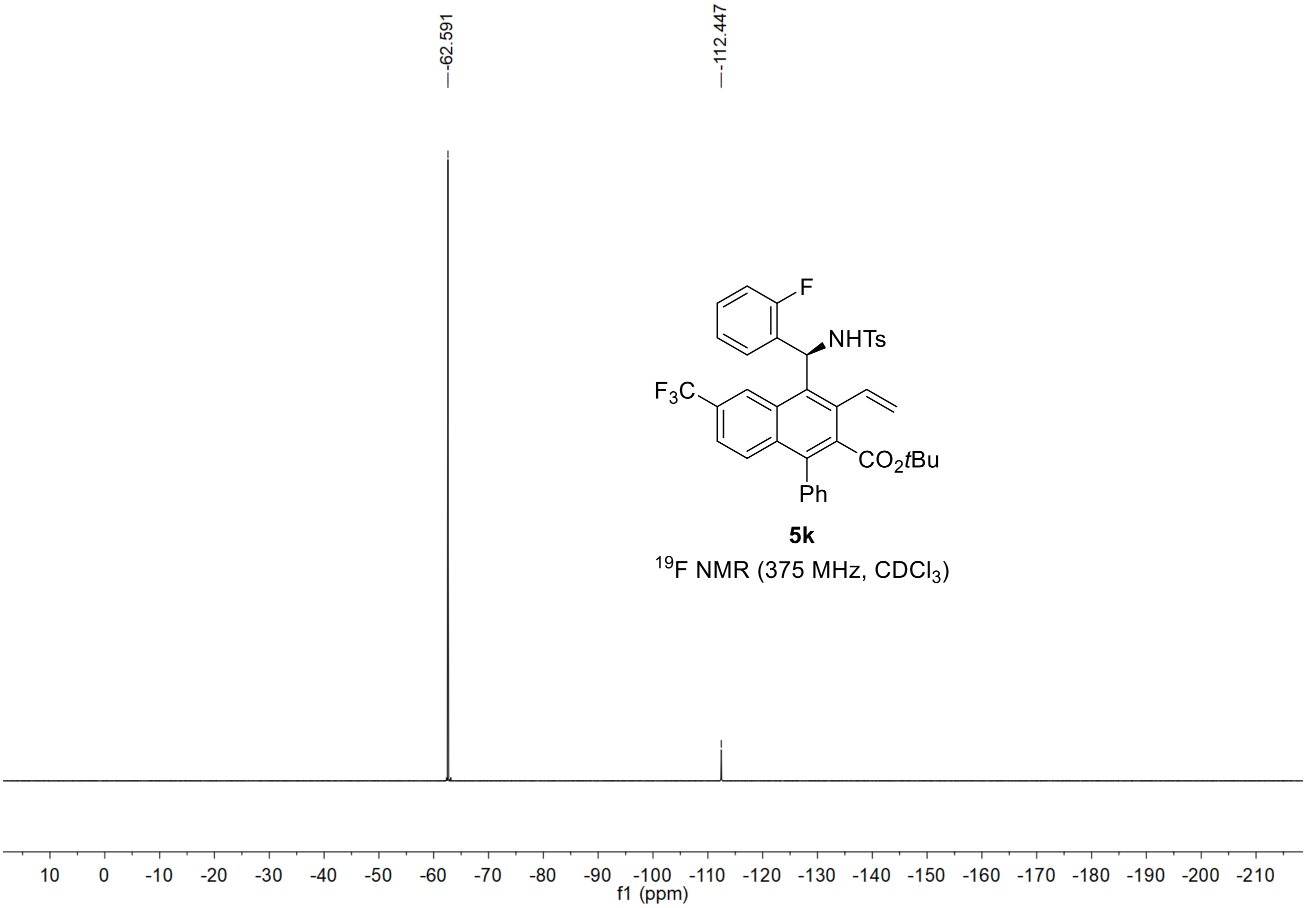
**5k**

$^1$H NMR (400 MHz, CDCl$_3$)



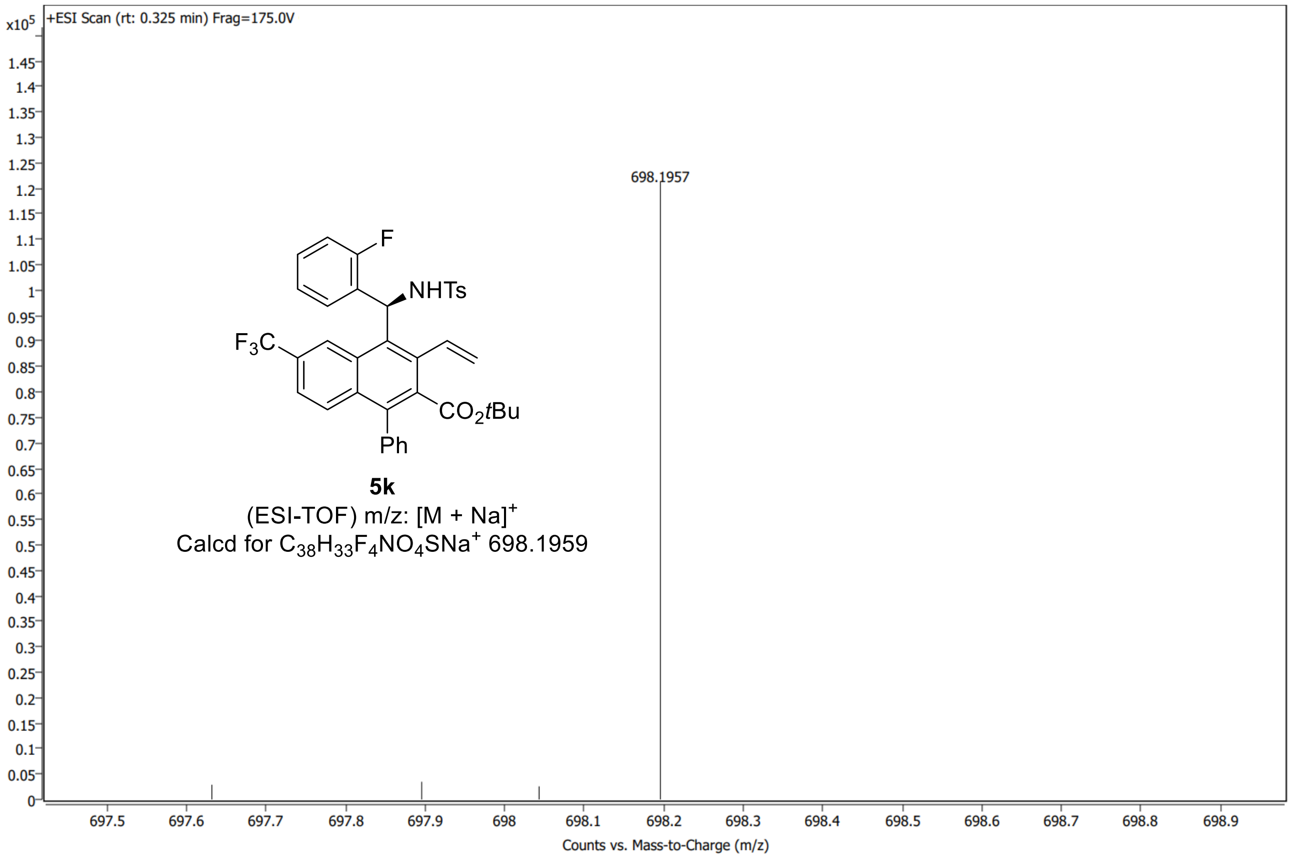
**5k**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**5k**

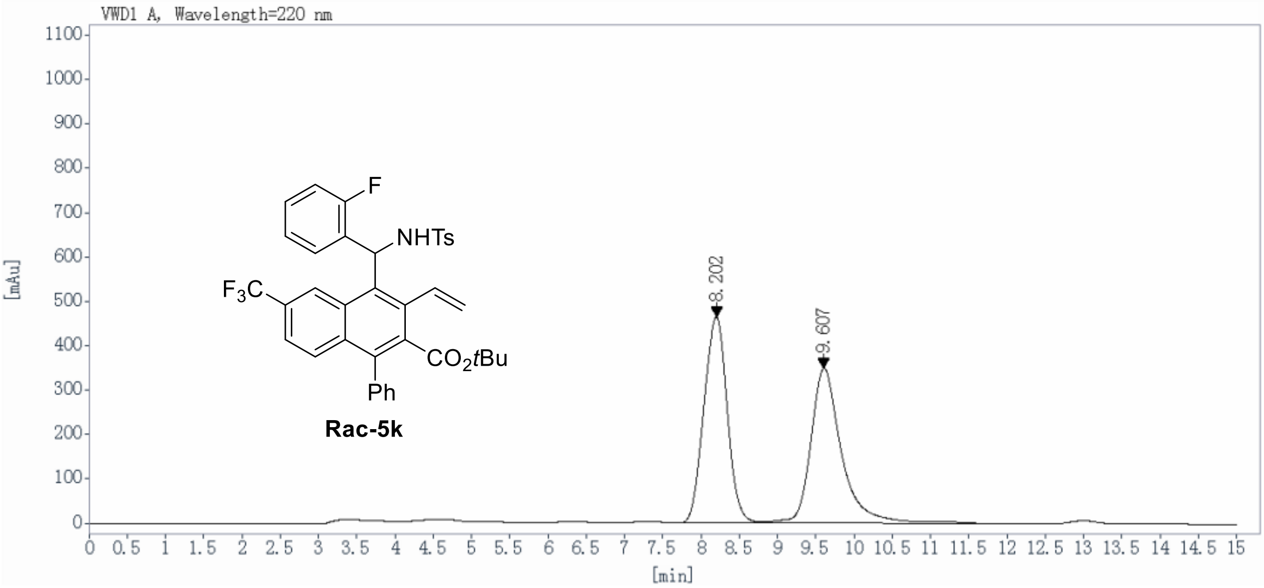
$^{19}F$ NMR (375 MHz, $CDCl_3$)



**5k**

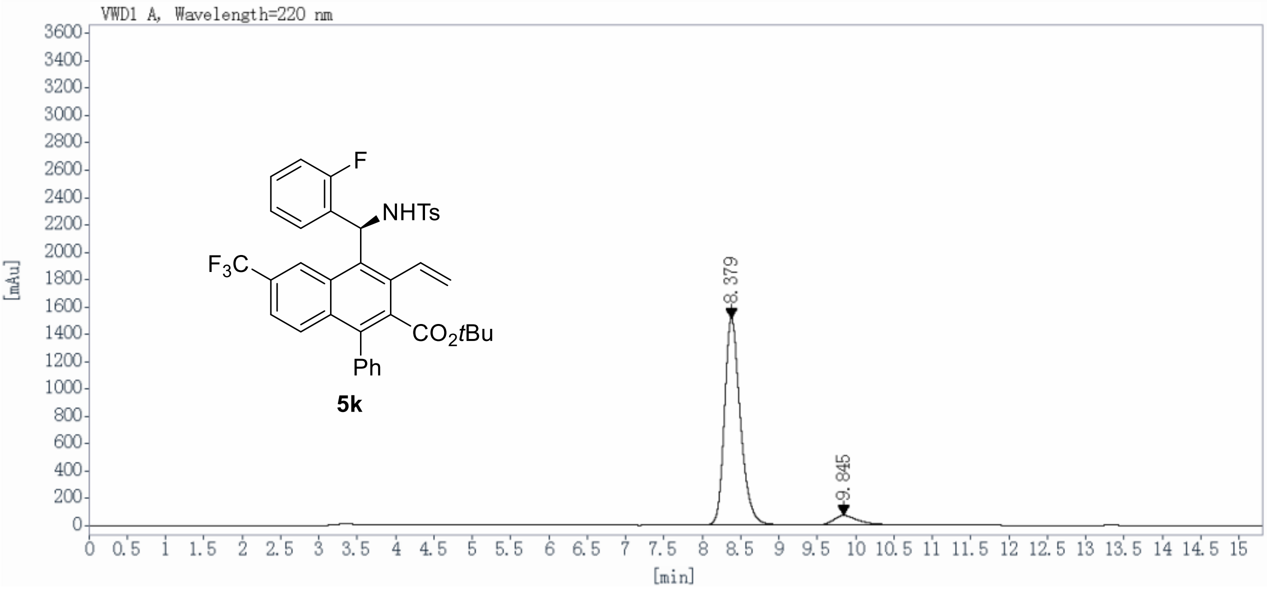
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{38}H_{33}F_4NO_4SNa^+$ 698.1959



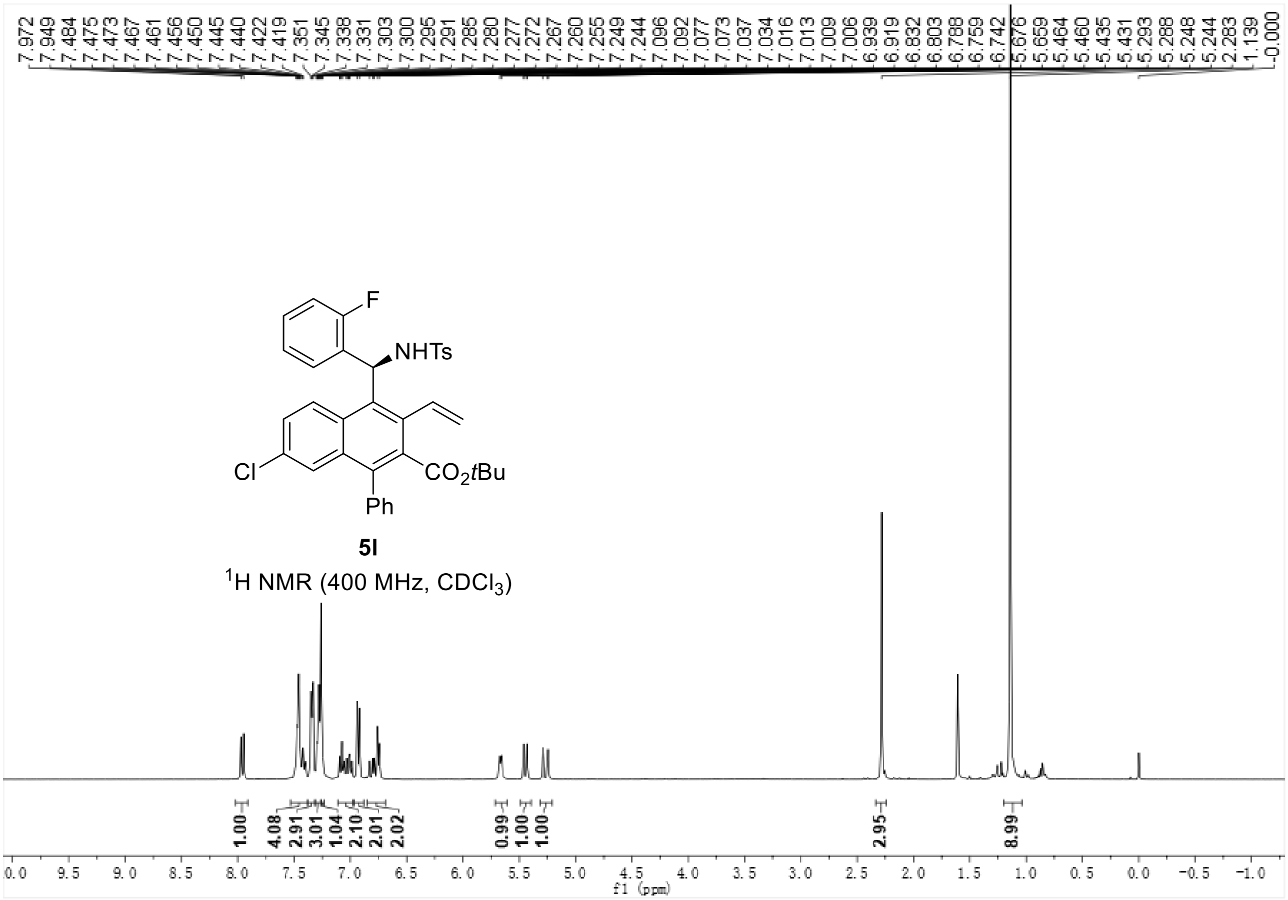
**Rac-5k**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.202 | BV | 0.34 | 464.1207 | 9875.3887 | 50.0727 |
| 9.607 | VV R | 0.42 | 348.8387 | 9846.7100 | 49.9273 |
| | | | Totals: | 19722.0986 | 100.0000 |



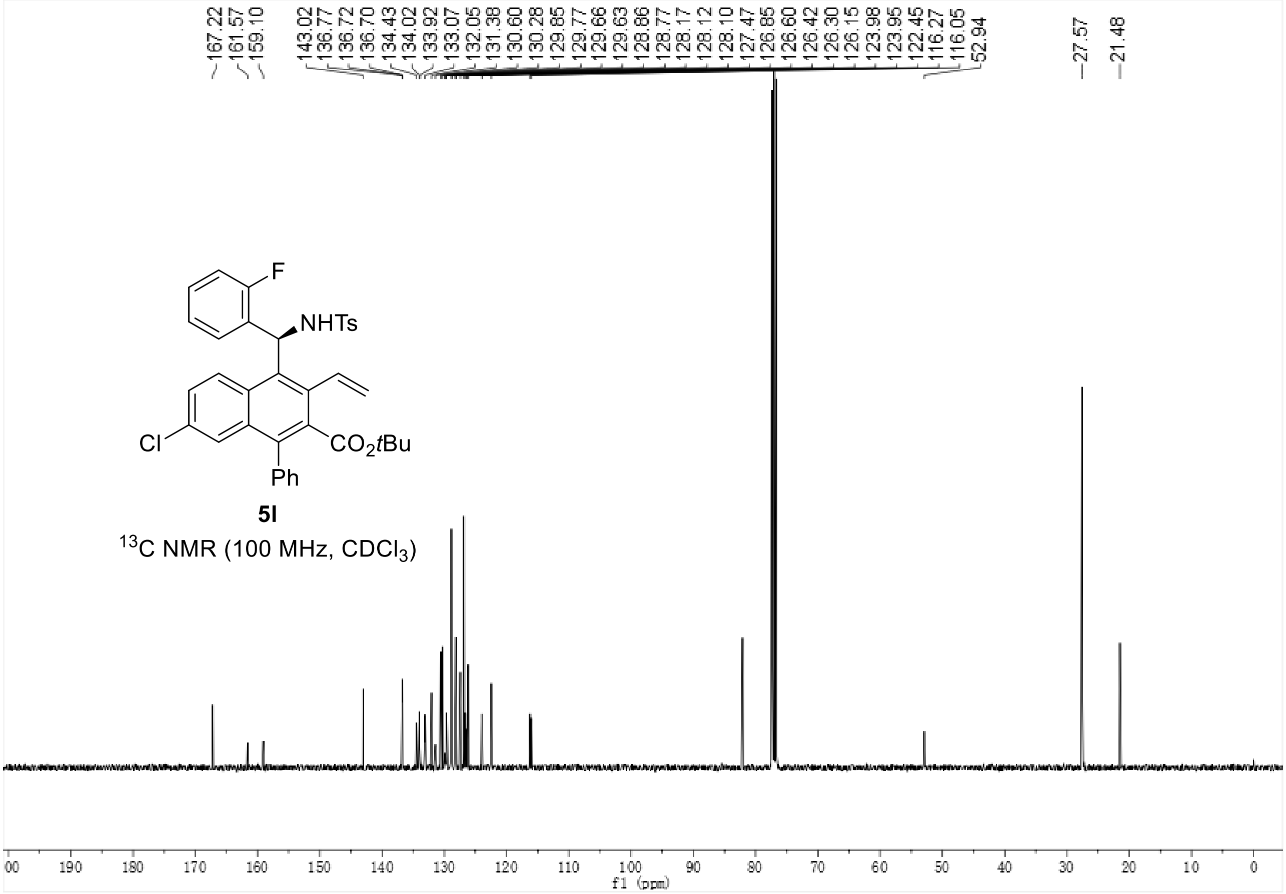
**5k**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.379 | BBA | 0.22 | 1514.4275 | 21907.9297 | 93.5985 |
| 9.845 | BBA | 0.34 | 67.9740 | 1498.3434 | 6.4015 |
| | | | Totals: | 23406.2731 | 100.0000 |



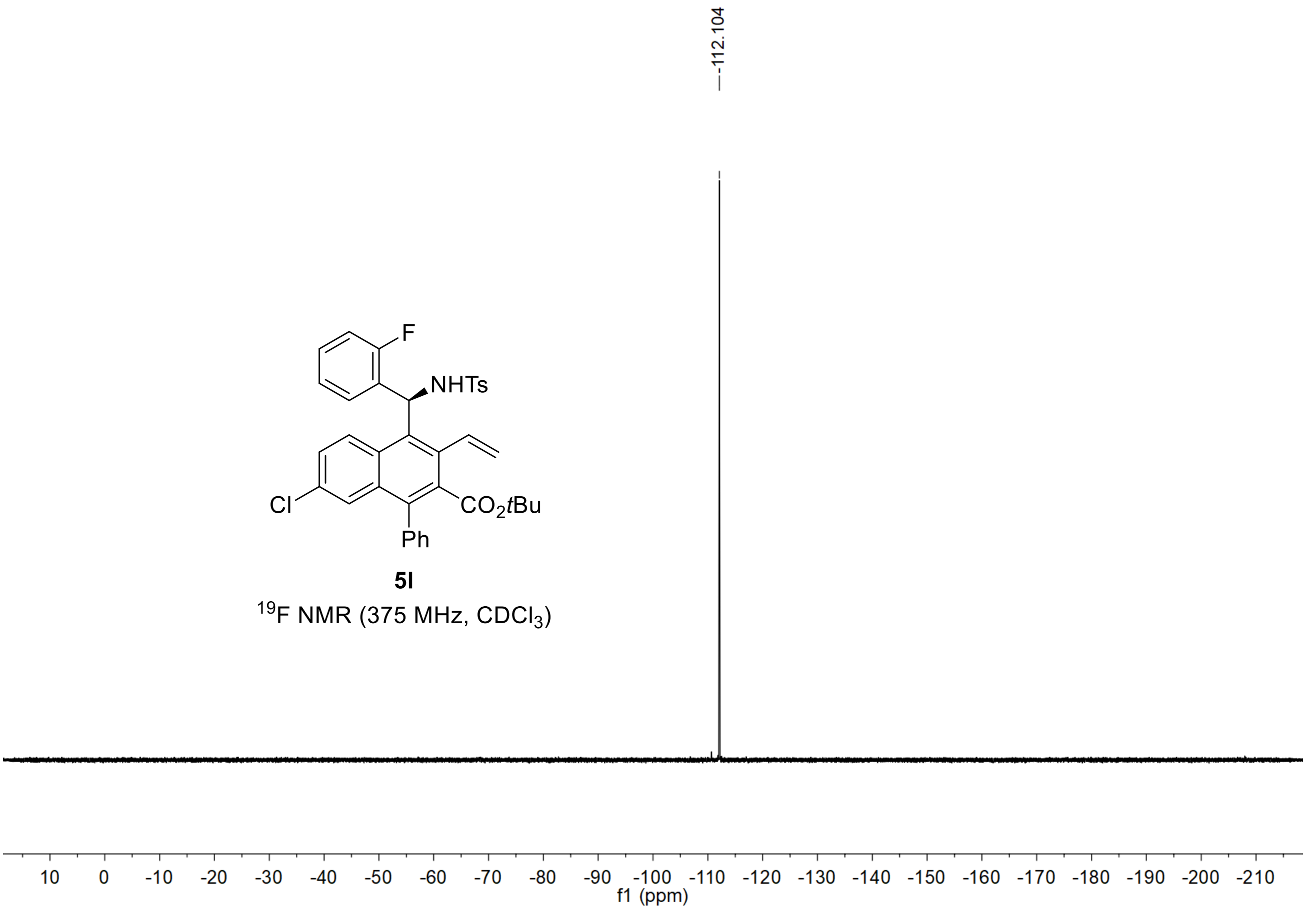
**5l**

$^1$H NMR (400 MHz, CDCl$_3$)



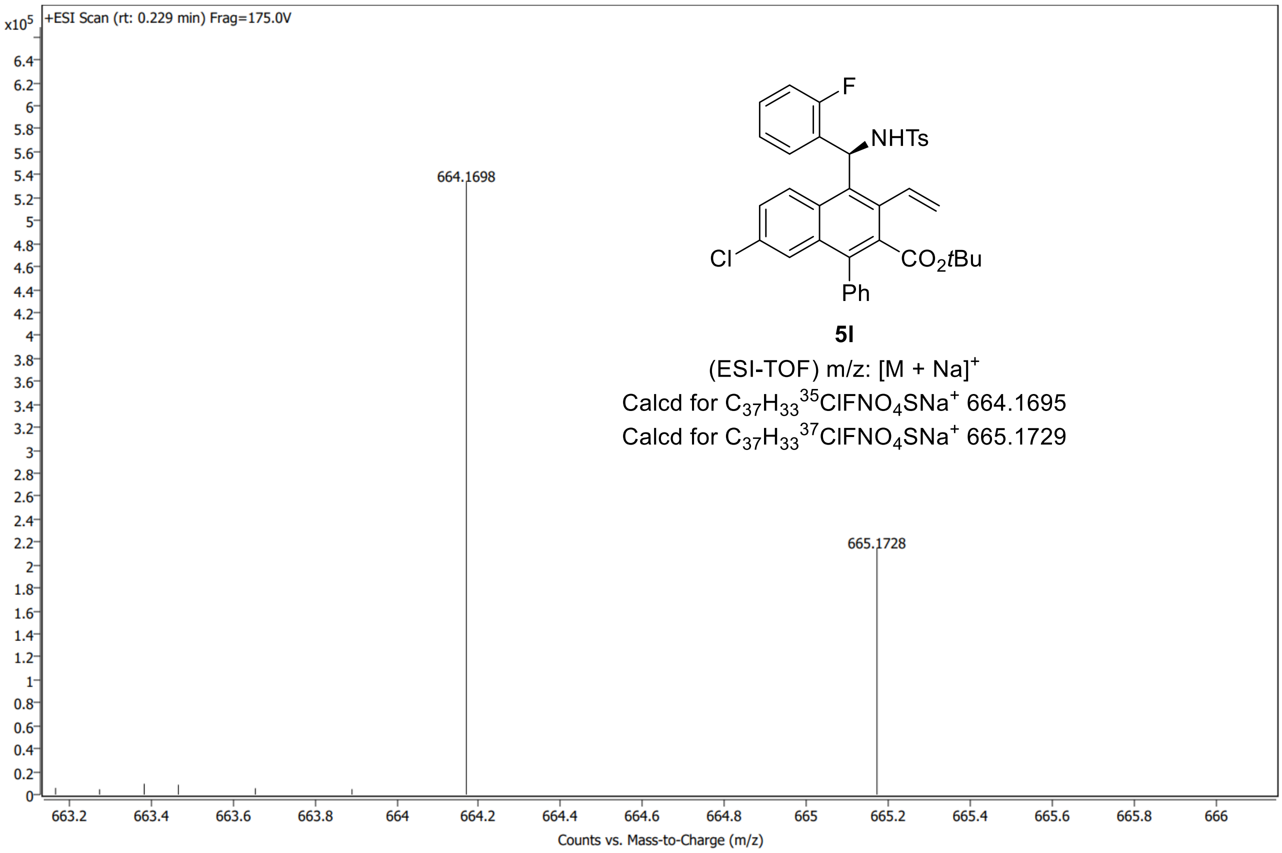
**5l**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**5l**

$^{19}$F NMR (375 MHz, $CDCl_3$)

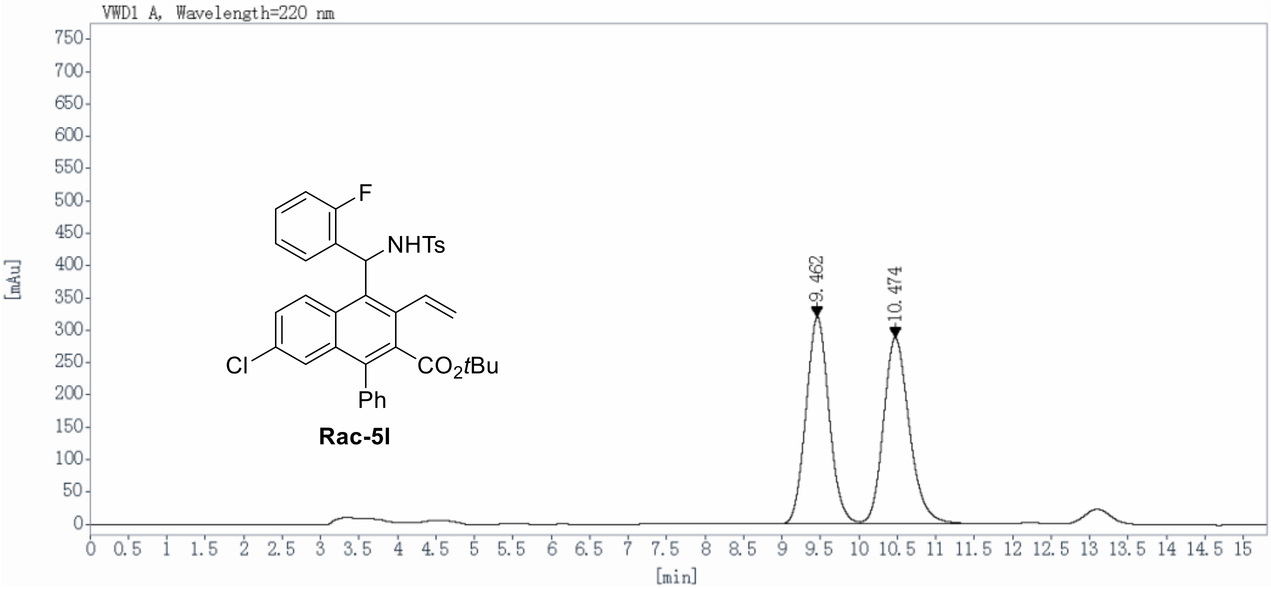


**5l**

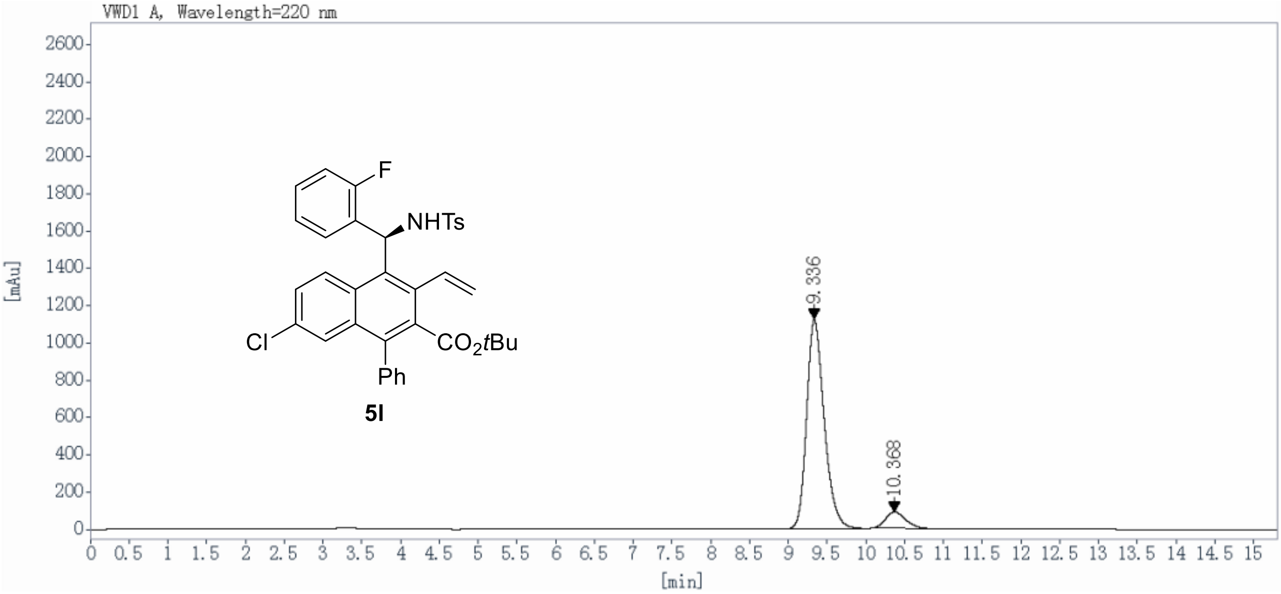
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{37}H_{33}{}^{35}ClFNO_4SNa^+$ 664.1695

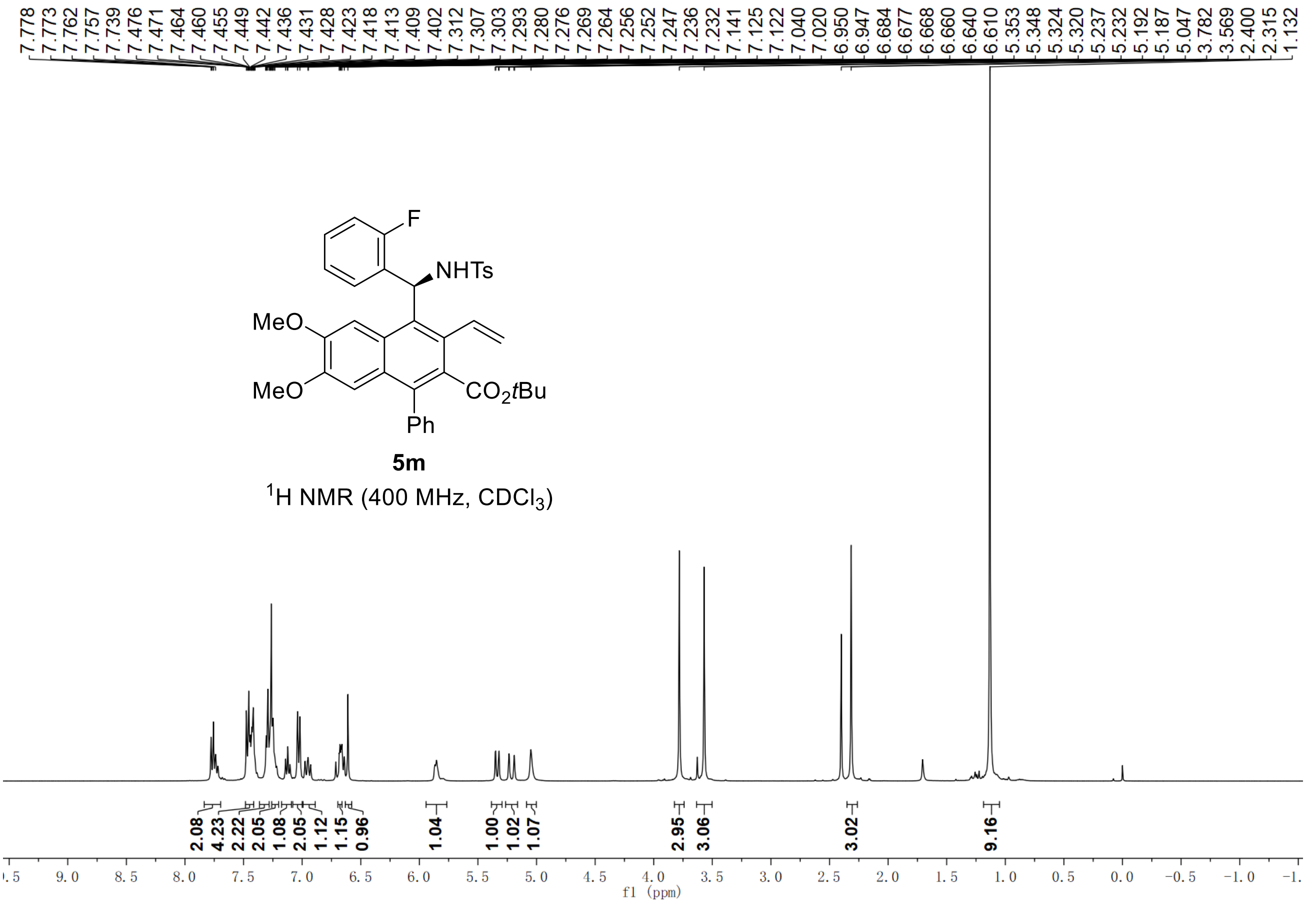
Calcd for $C_{37}H_{33}{}^{37}ClFNO_4SNa^+$ 665.1729



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.462 | VV R | 0.33 | 320.2312 | 6746.8213 | 49.7404 |
| 10.474 | VB | 0.36 | 289.0894 | 6817.2397 | 50.2596 |
|  |  |  | Totals: | 13564.0610 | 100.0000 |

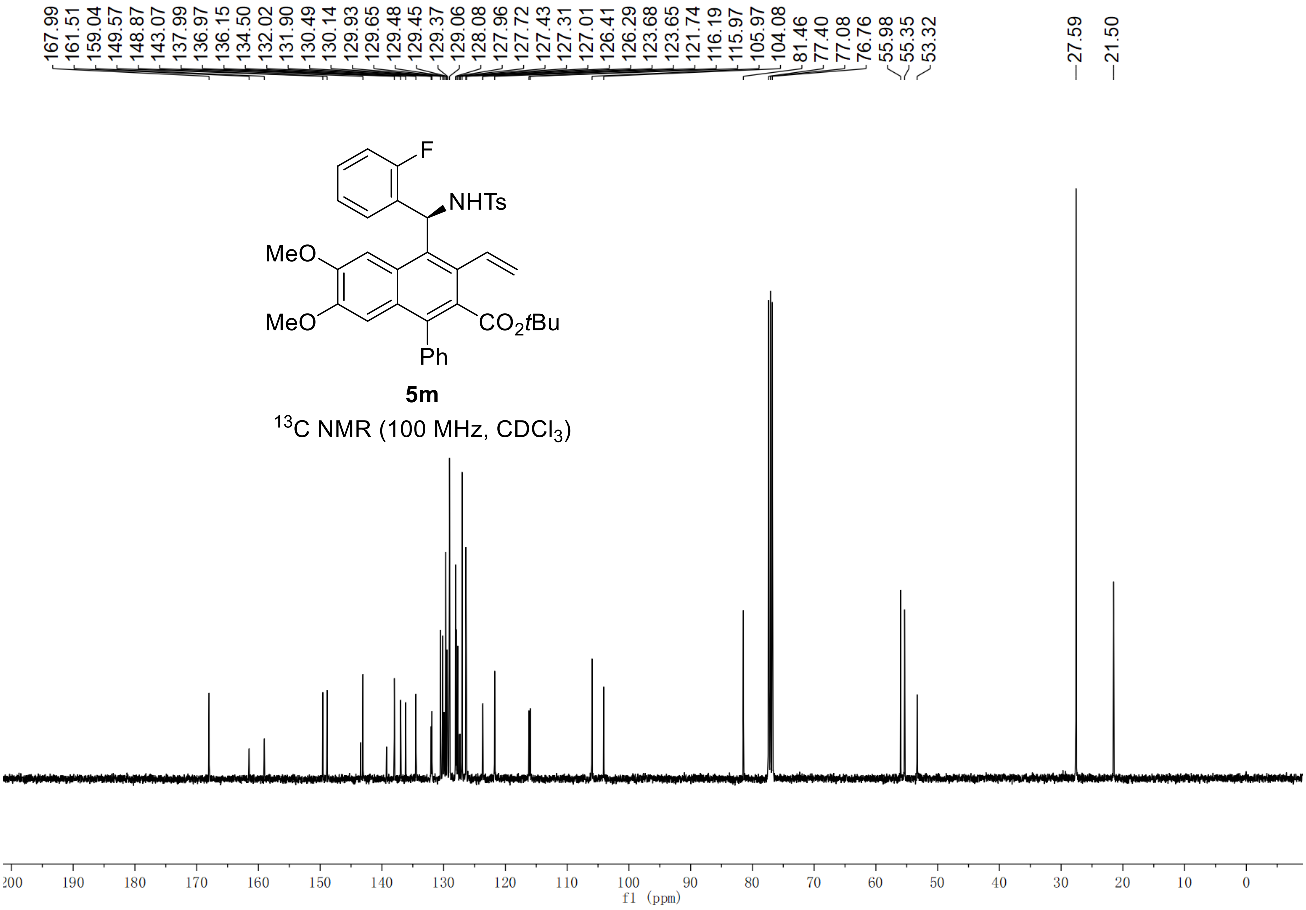


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.336 | BB | 0.24 | 1123.1202 | 17779.9023 | 91.5730 |
| 10.368 | BBA | 0.28 | 88.5395 | 1636.1914 | 8.4270 |
|  |  |  | Totals: | 19416.0938 | 100.0000 |



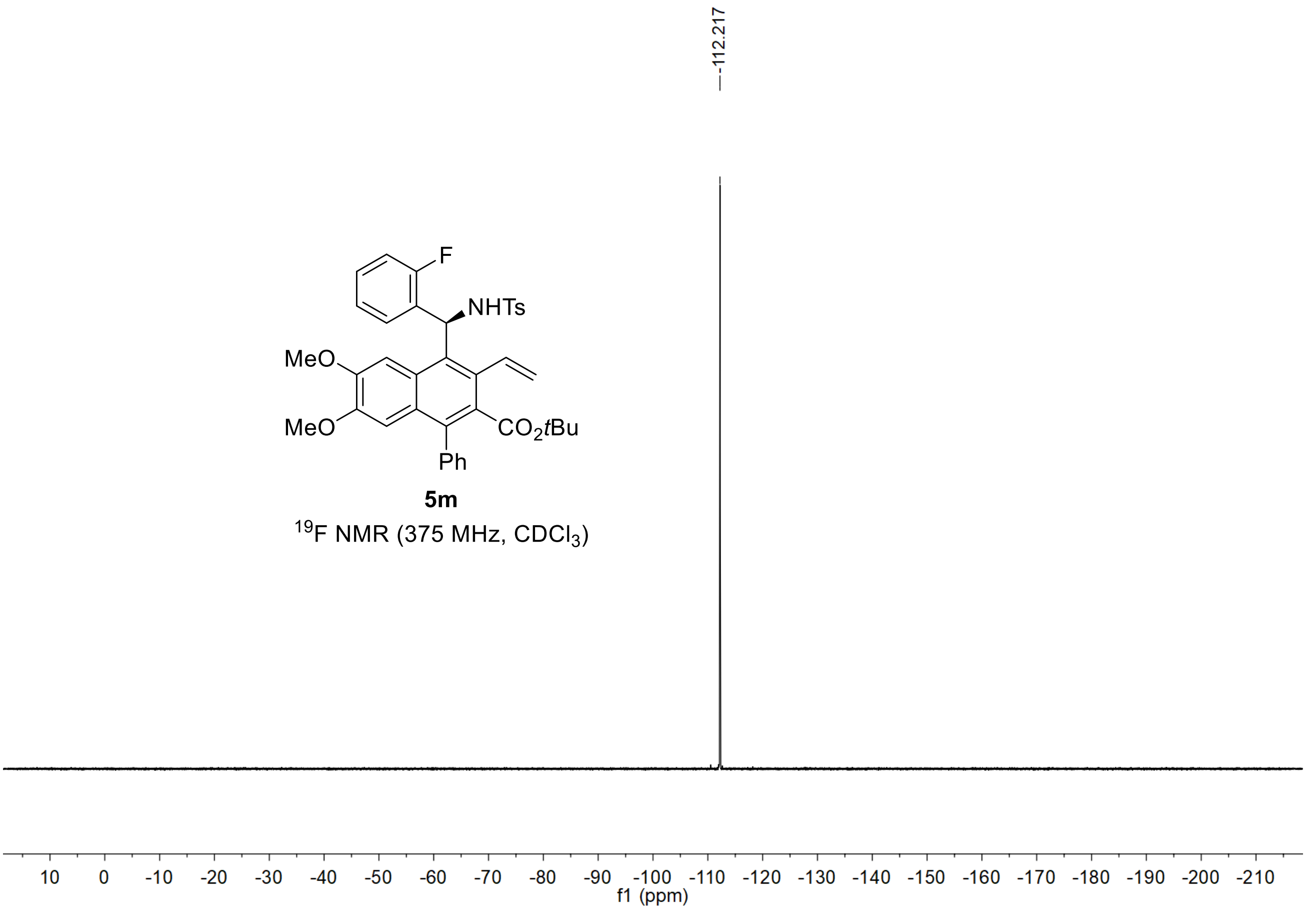
**5m**

$^1$H NMR (400 MHz, CDCl$_3$)



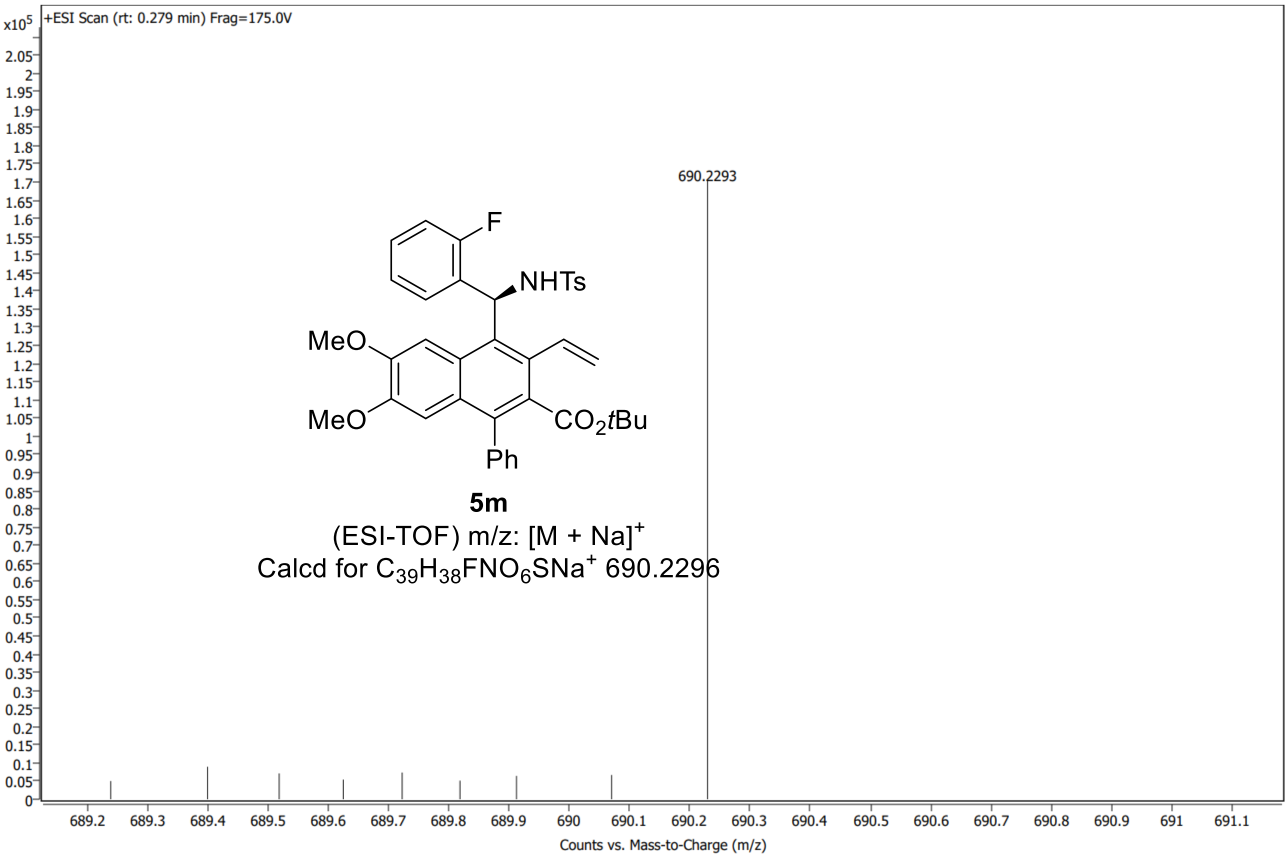
**5m**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**5m**

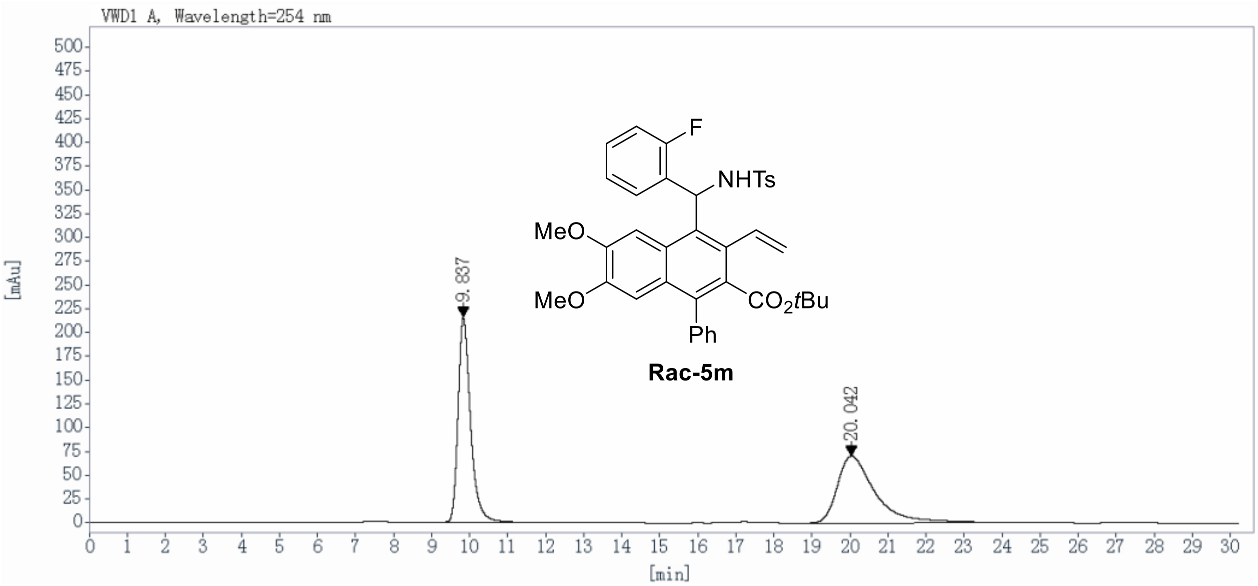
$^{19}$F NMR (375 MHz, $CDCl_3$)



**5m**

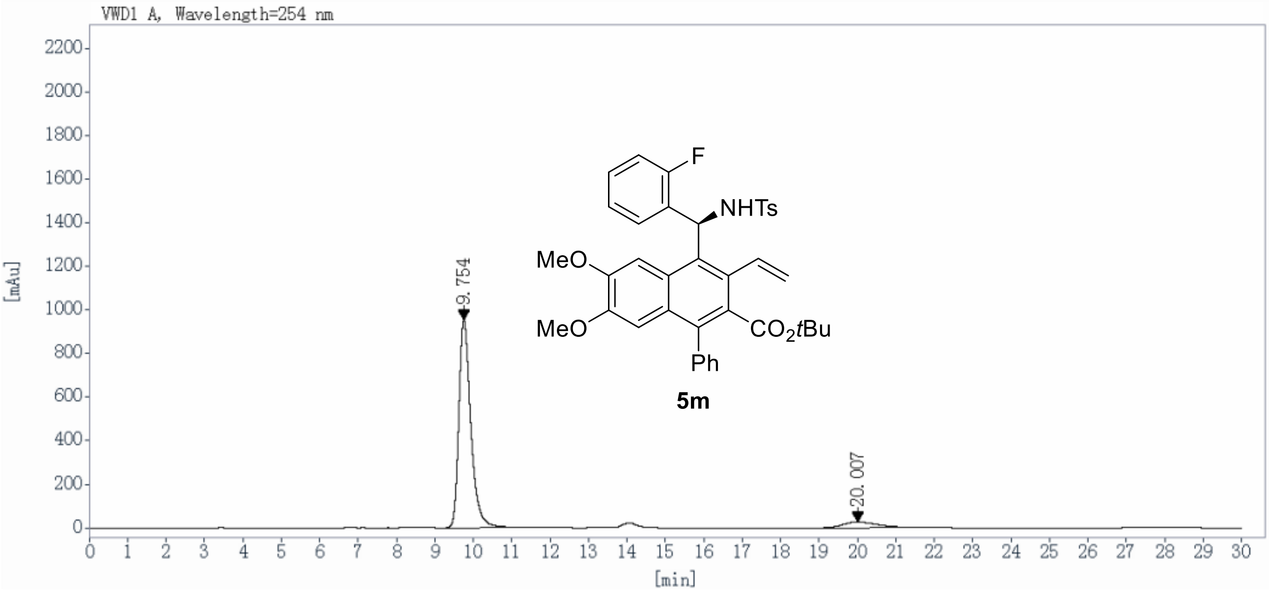
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{39}H_{38}FNO_6SNa^+$ 690.2296



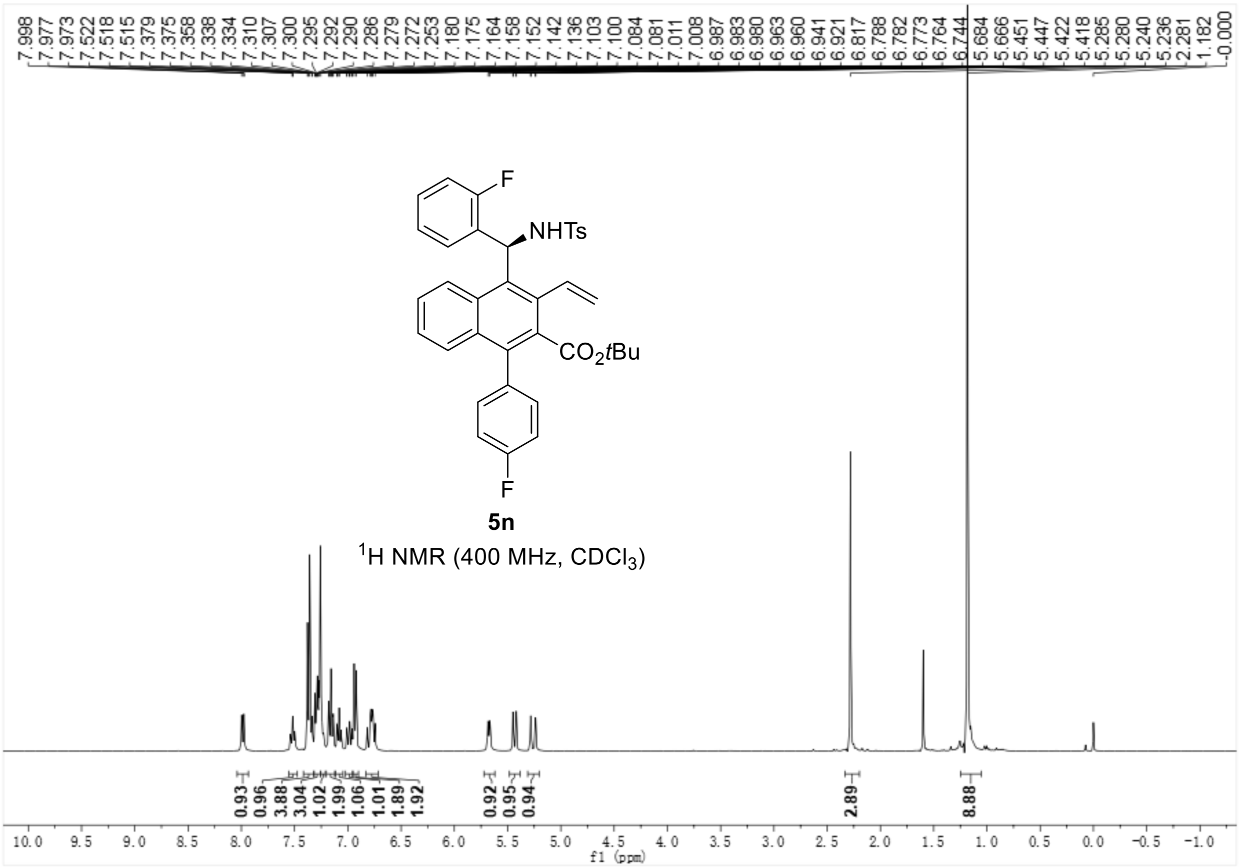
**Rac-5m**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.837 | BBA | 0.34 | 215.5876 | 4911.1758 | 50.2053 |
| 20.042 | BBA | 1.03 | 70.3176 | 4871.0068 | 49.7947 |
| | | | Totals: | 9782.1826 | 100.0000 |



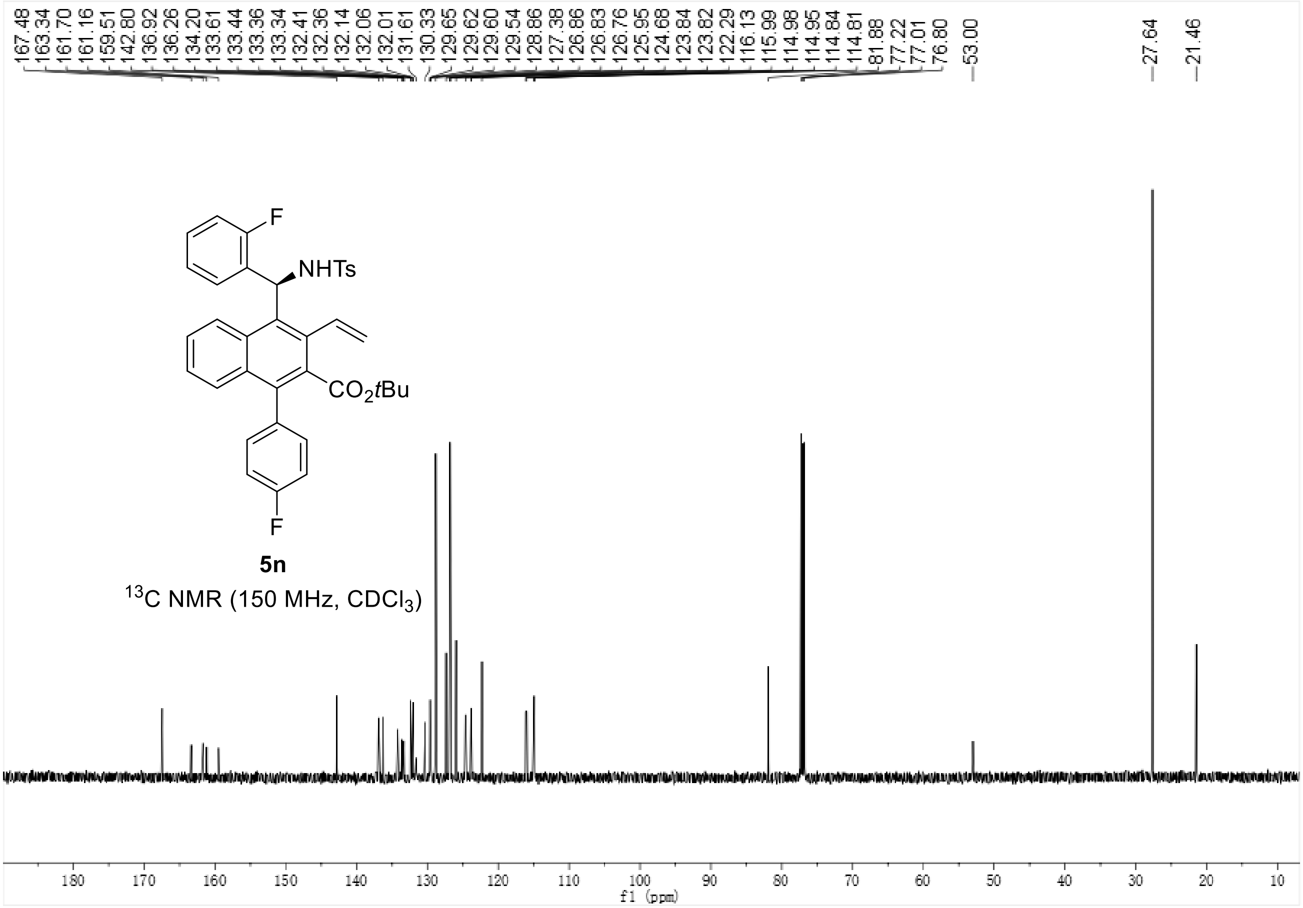
**5m**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 9.754 | BB | 0.32 | 954.0012 | 20439.1855 | 92.3151 |
| 20.007 | BBA | 0.96 | 26.7394 | 1701.4841 | 7.6849 |
| | | | Totals: | 22140.6697 | 100.0000 |



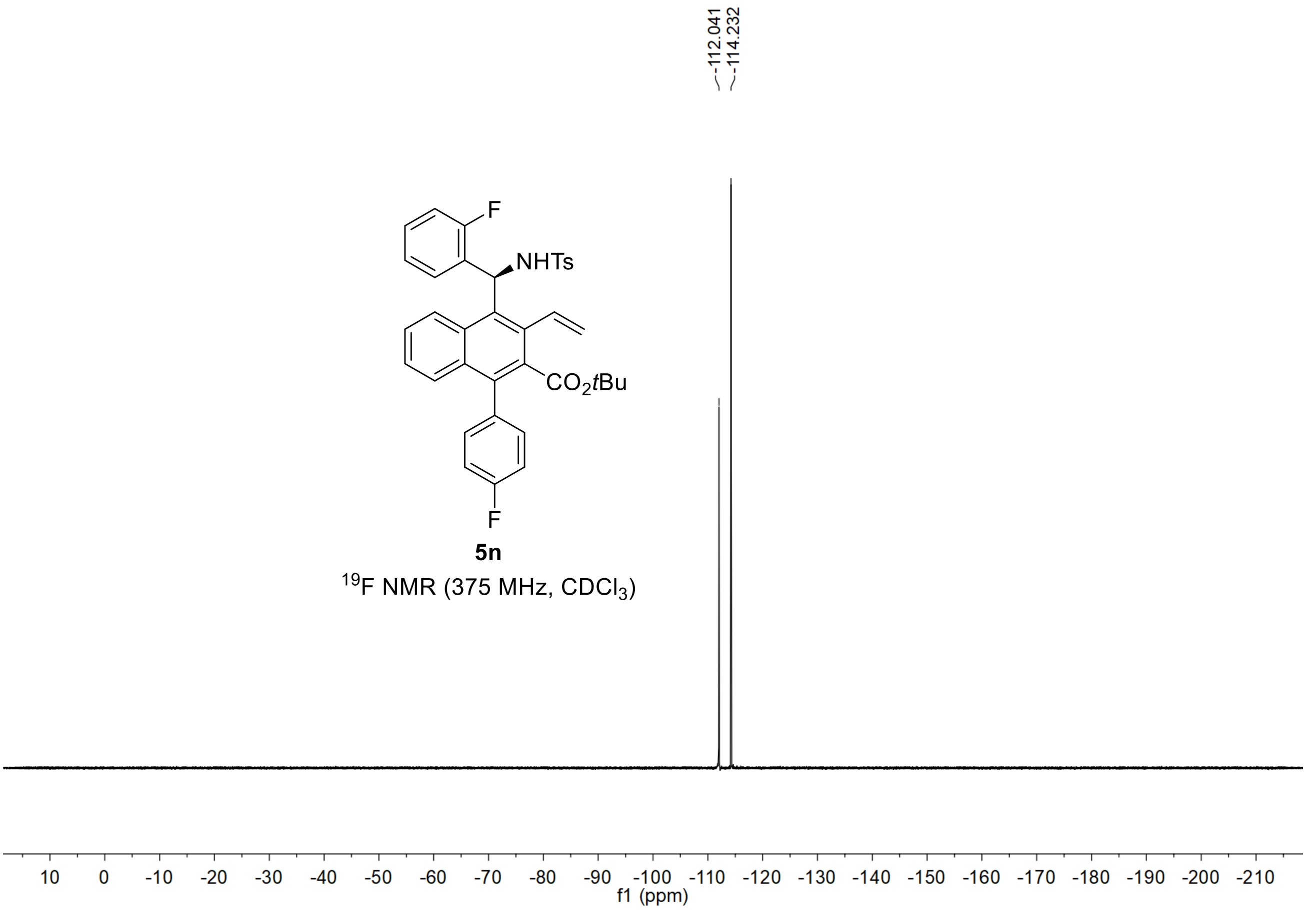
**5n**

$^1$H NMR (400 MHz, CDCl$_3$)



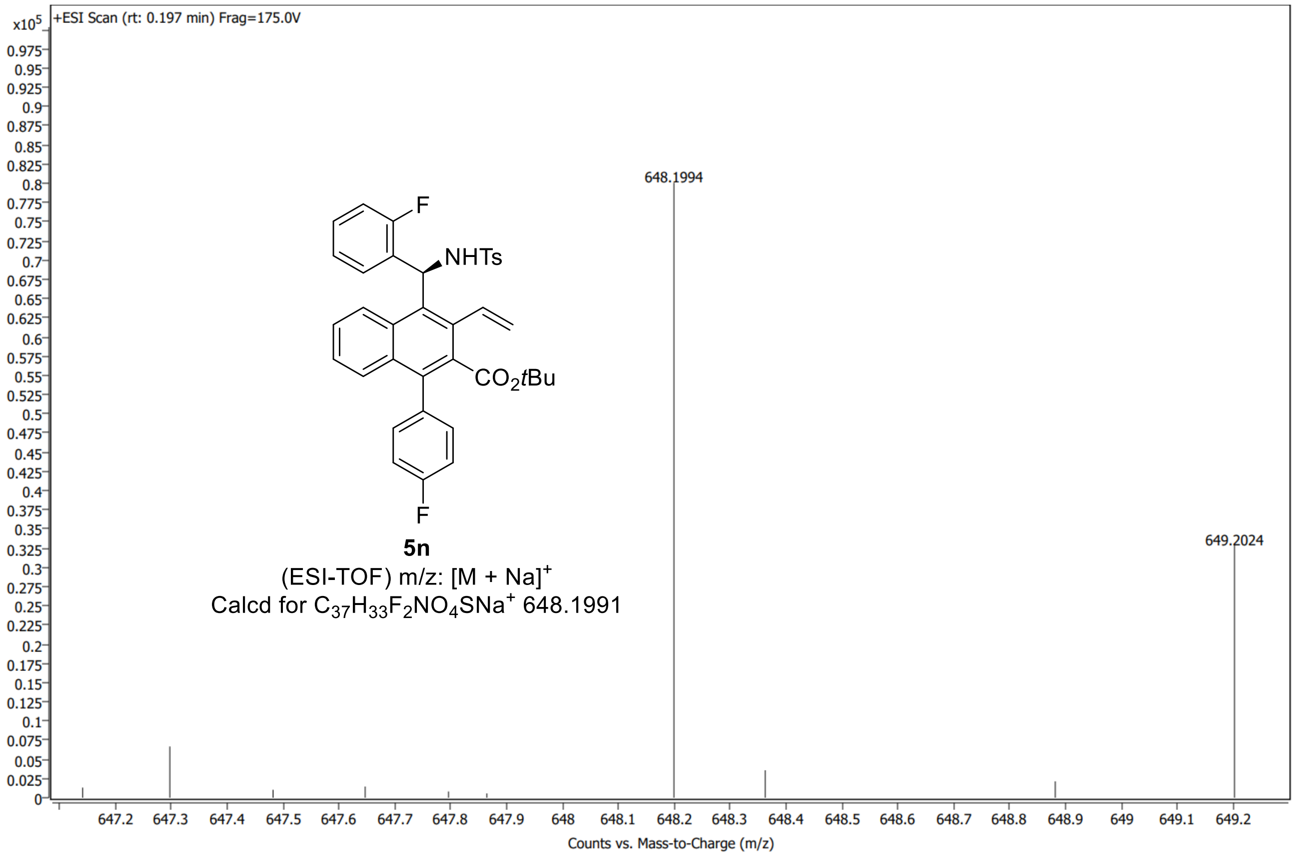
**5n**

$^{13}$C NMR (150 MHz, CDCl$_3$)



**5n**

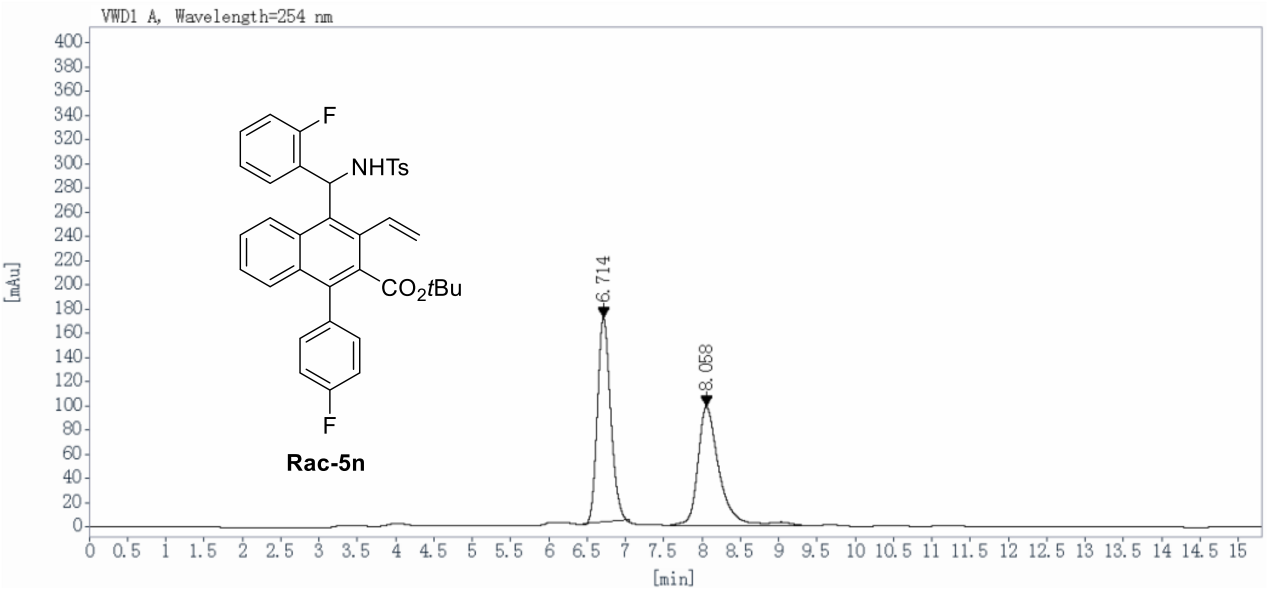
$^{19}$F NMR (375 MHz, $CDCl_3$)



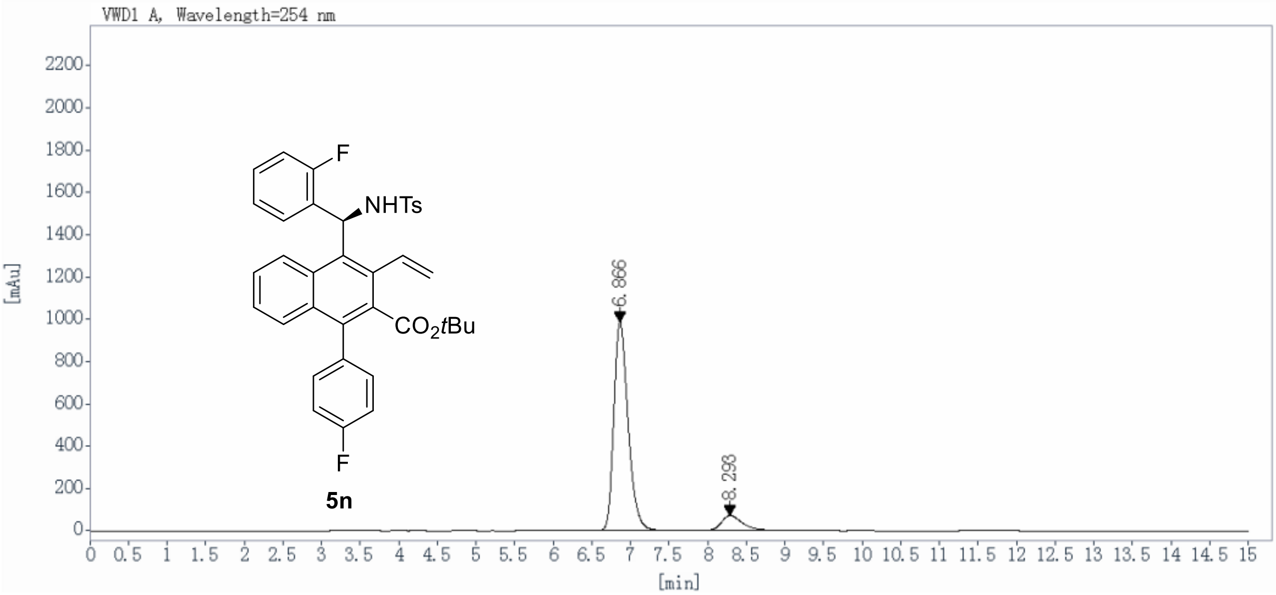
**5n**

(ESI-TOF) m/z: $[M + Na]^+$

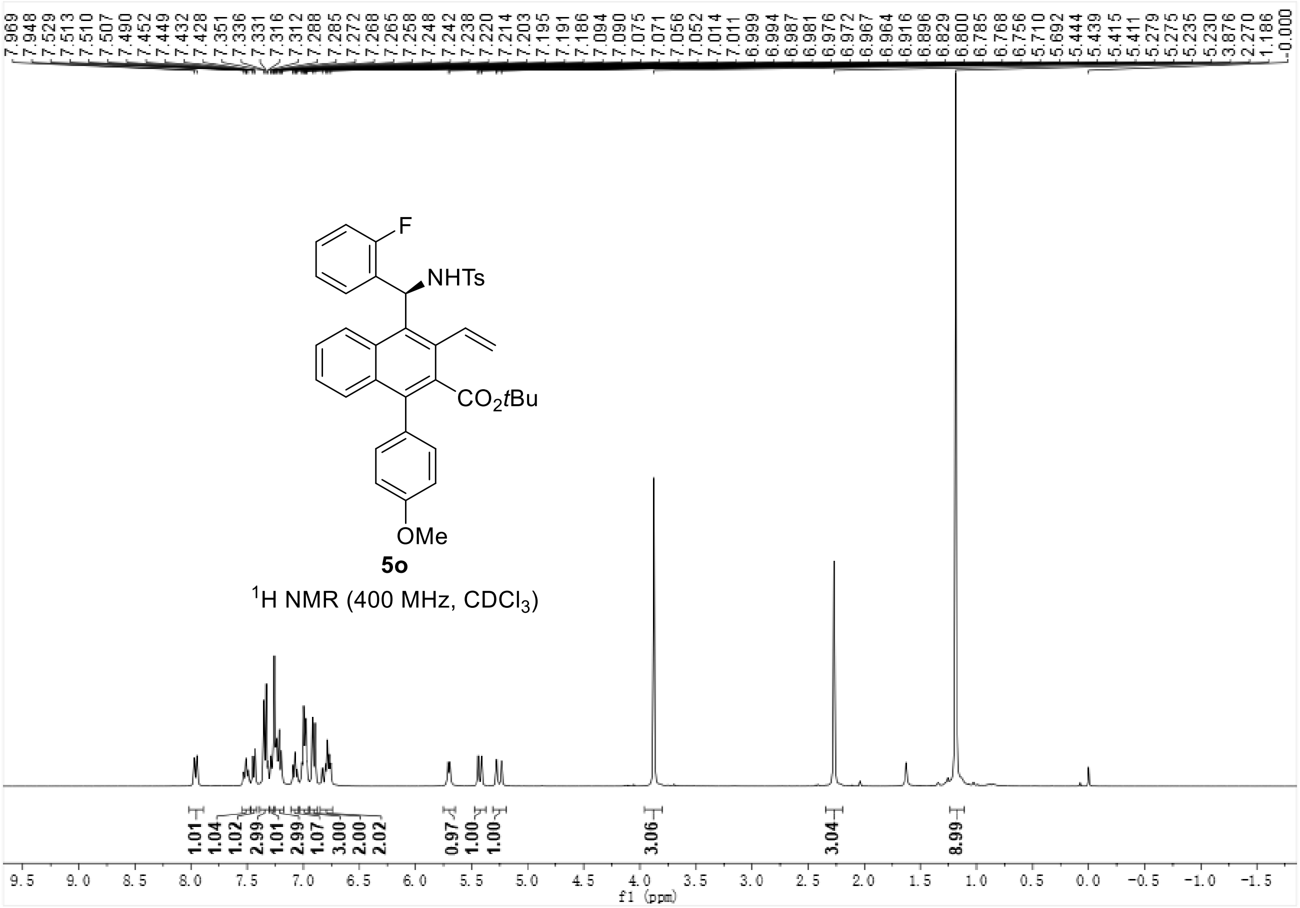
Calcd for $C_{37}H_{33}F_2NO_4SNa^+$ 648.1991



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.714 | MM | 0.20 | 168.9042 | 2003.1720 | 50.9783 |
| 8.058 | BV R | 0.28 | 98.3440 | 1926.2898 | 49.0217 |
|  |  |  | Totals: | 3929.4618 | 100.0000 |

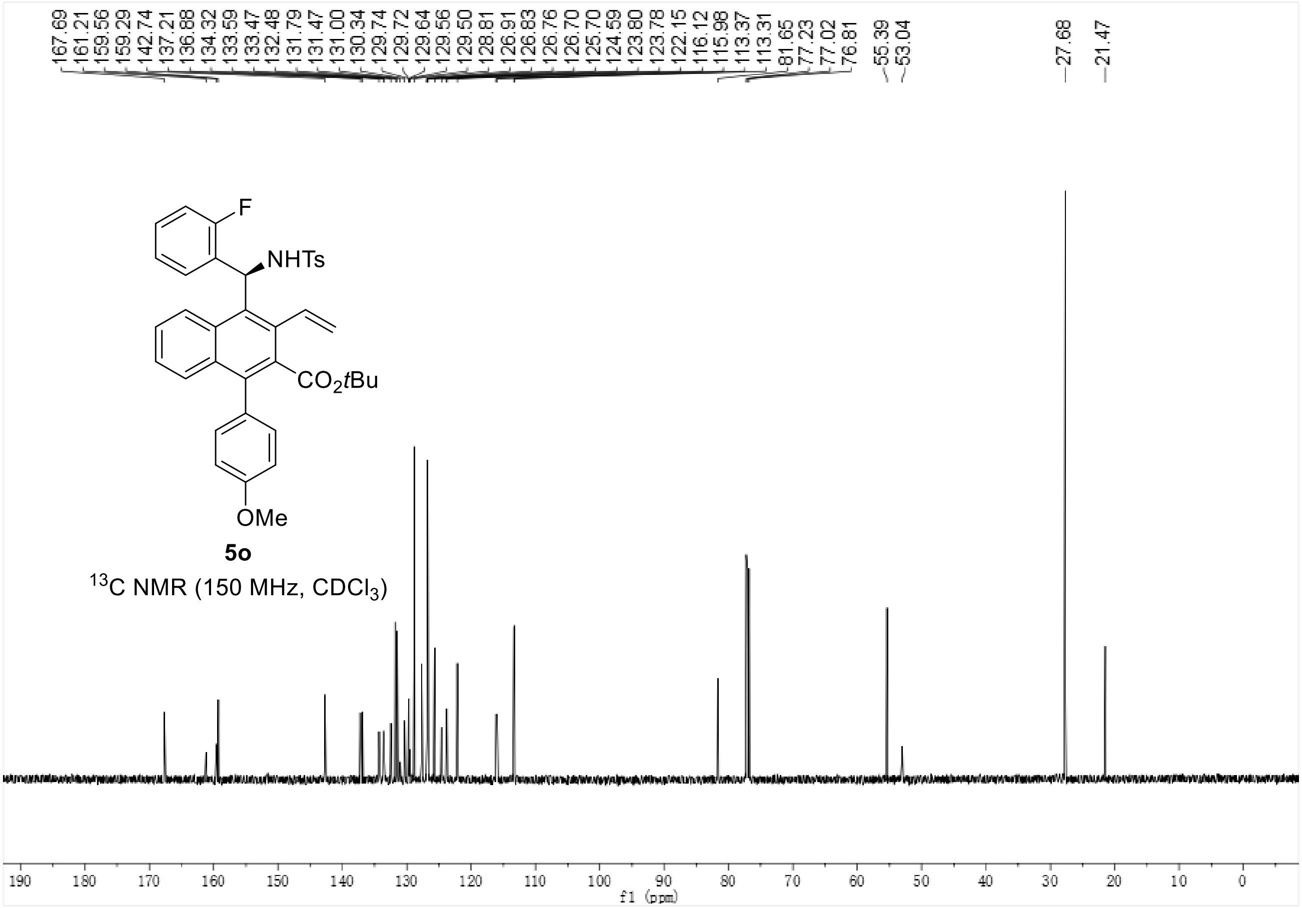


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.866 | BV R | 0.20 | 987.6791 | 12607.7207 | 90.9045 |
| 8.293 | BBA | 0.28 | 69.4877 | 1261.4764 | 9.0955 |
|  |  |  | Totals: | 13869.1971 | 100.0000 |



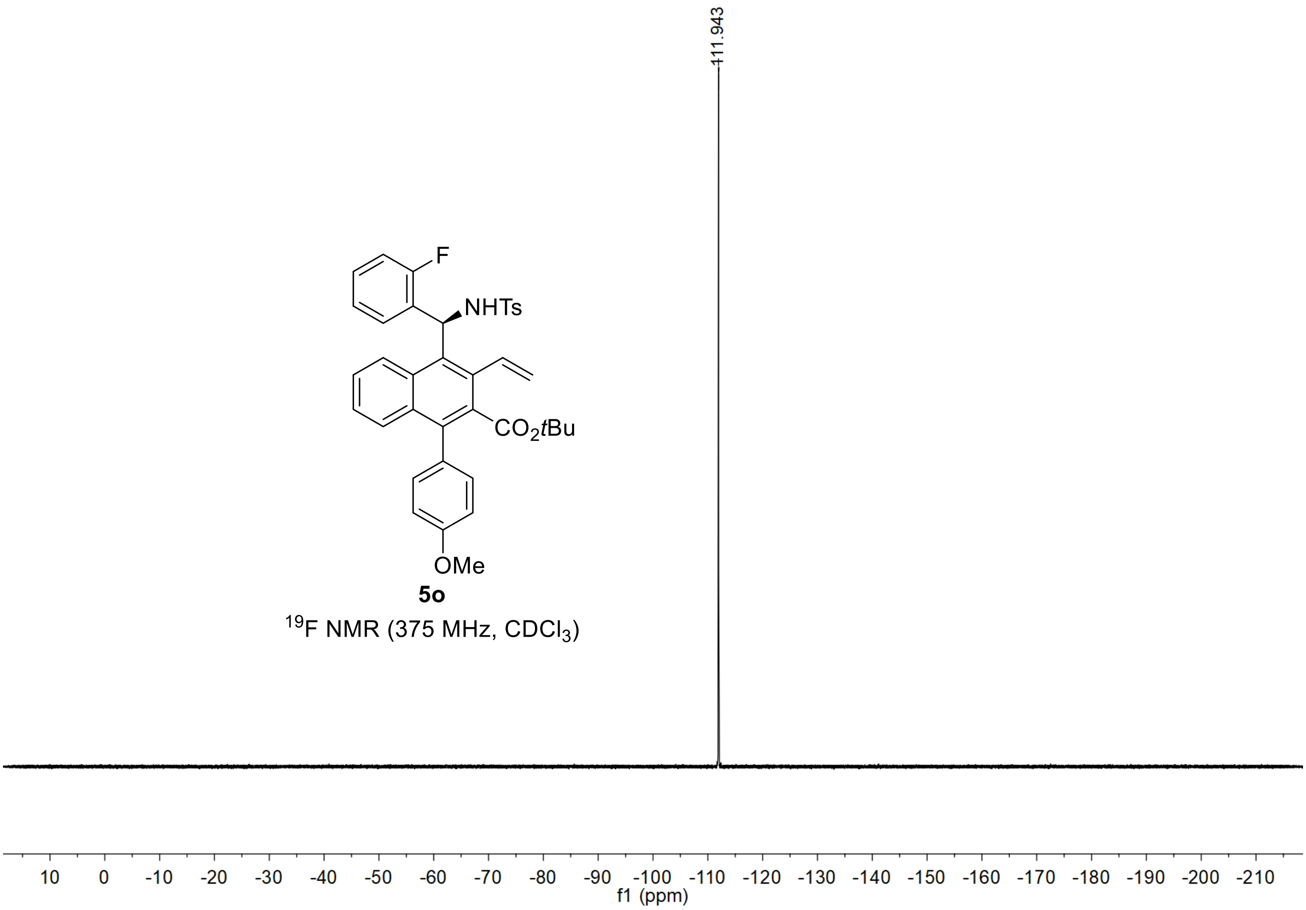
**5o**

$^1$H NMR (400 MHz, $CDCl_3$)



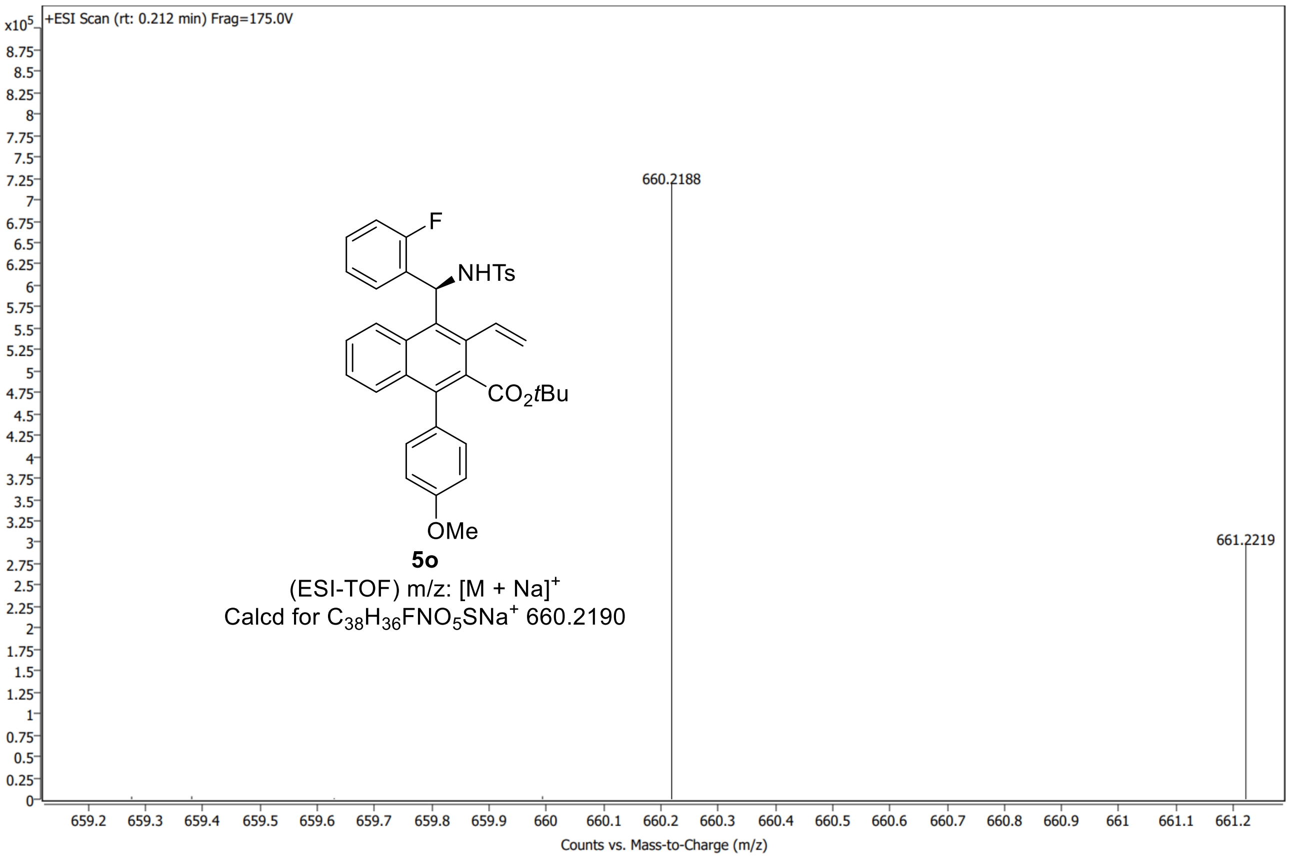
**5o**

$^{13}$C NMR (150 MHz, $CDCl_3$)



**5o**

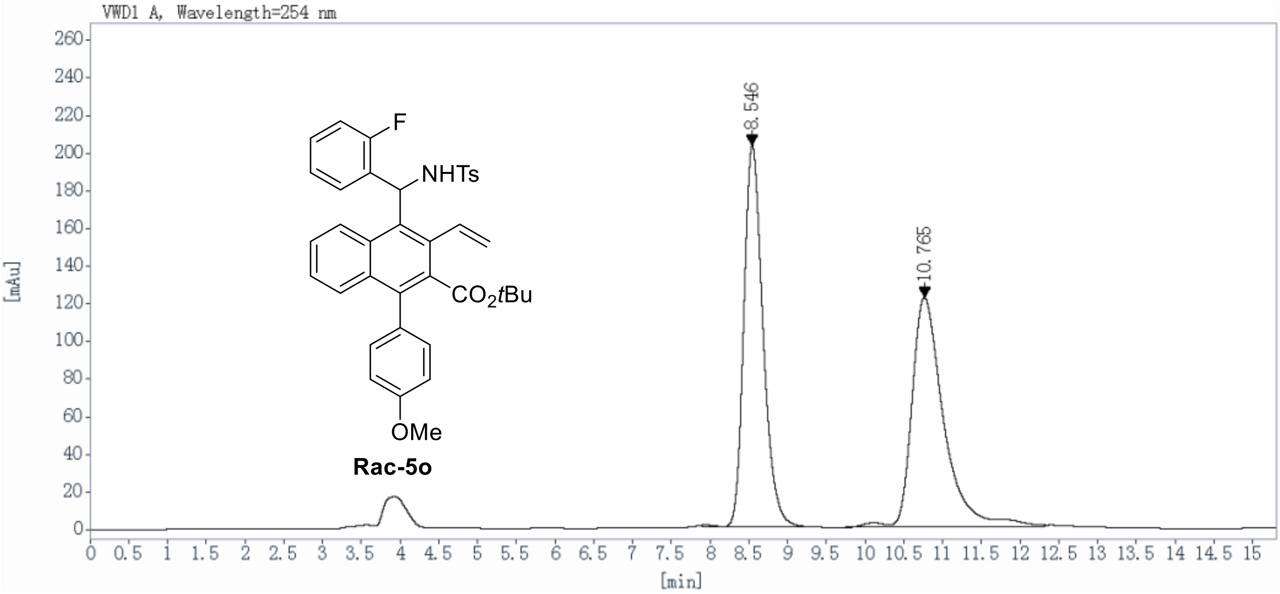
$^{19}$F NMR (375 MHz, $CDCl_3$)



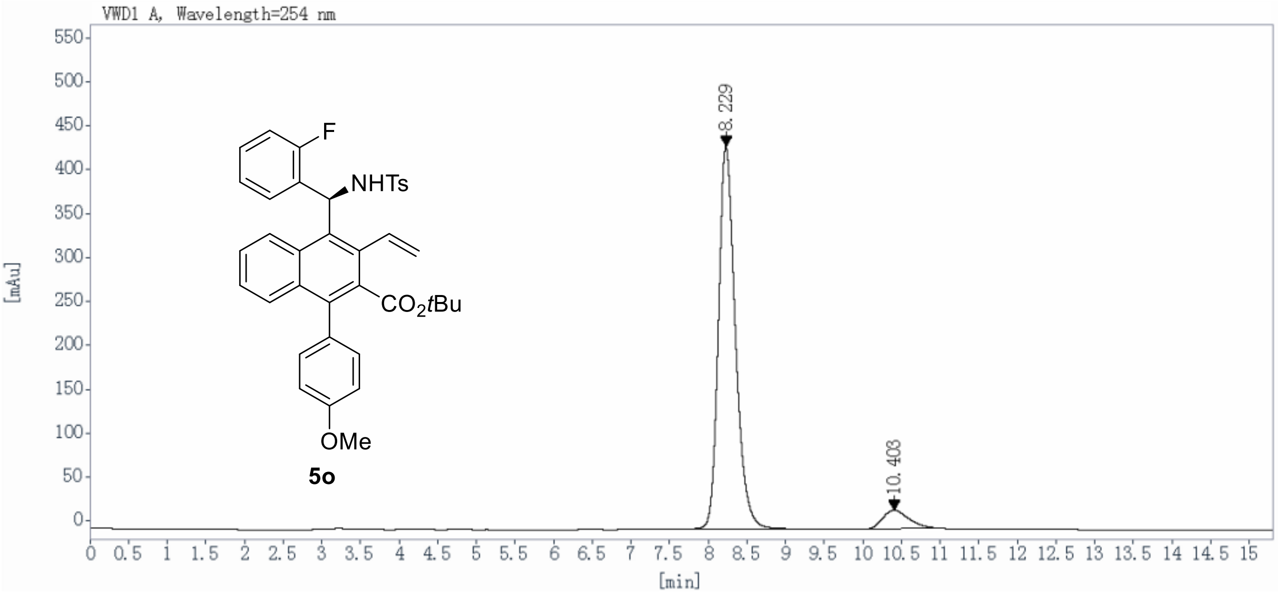
**5o**

(ESI-TOF) m/z: $[M + Na]^+$

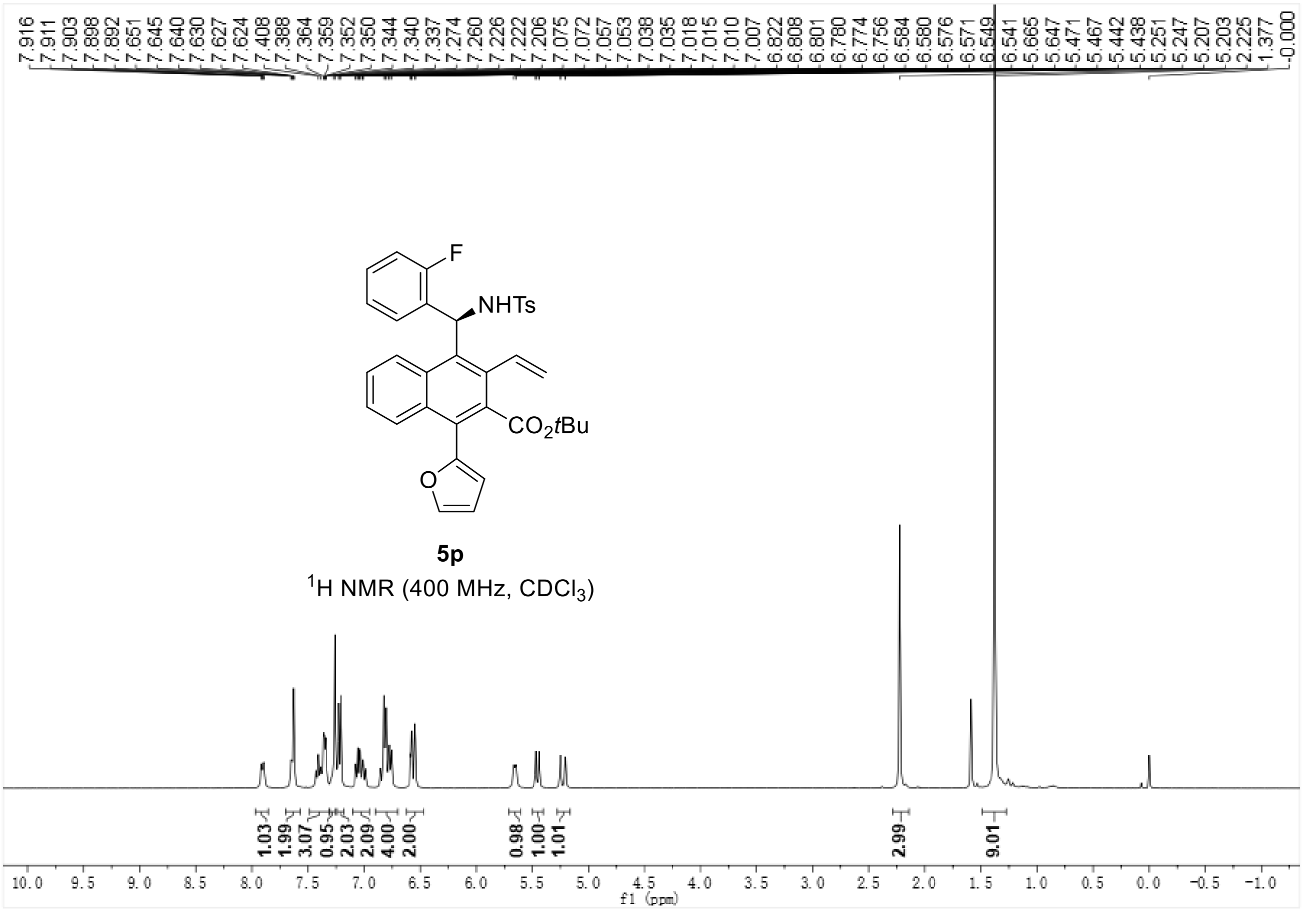
Calcd for $C_{38}H_{36}FNO_5SNa^+$ 660.2190



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.546 | MM | 0.28 | 202.5246 | 3456.7046 | 50.0380 |
| 10.765 | MM | 0.47 | 121.6565 | 3451.4490 | 49.9620 |
| | | | Totals: | 6908.1536 | 100.0000 |

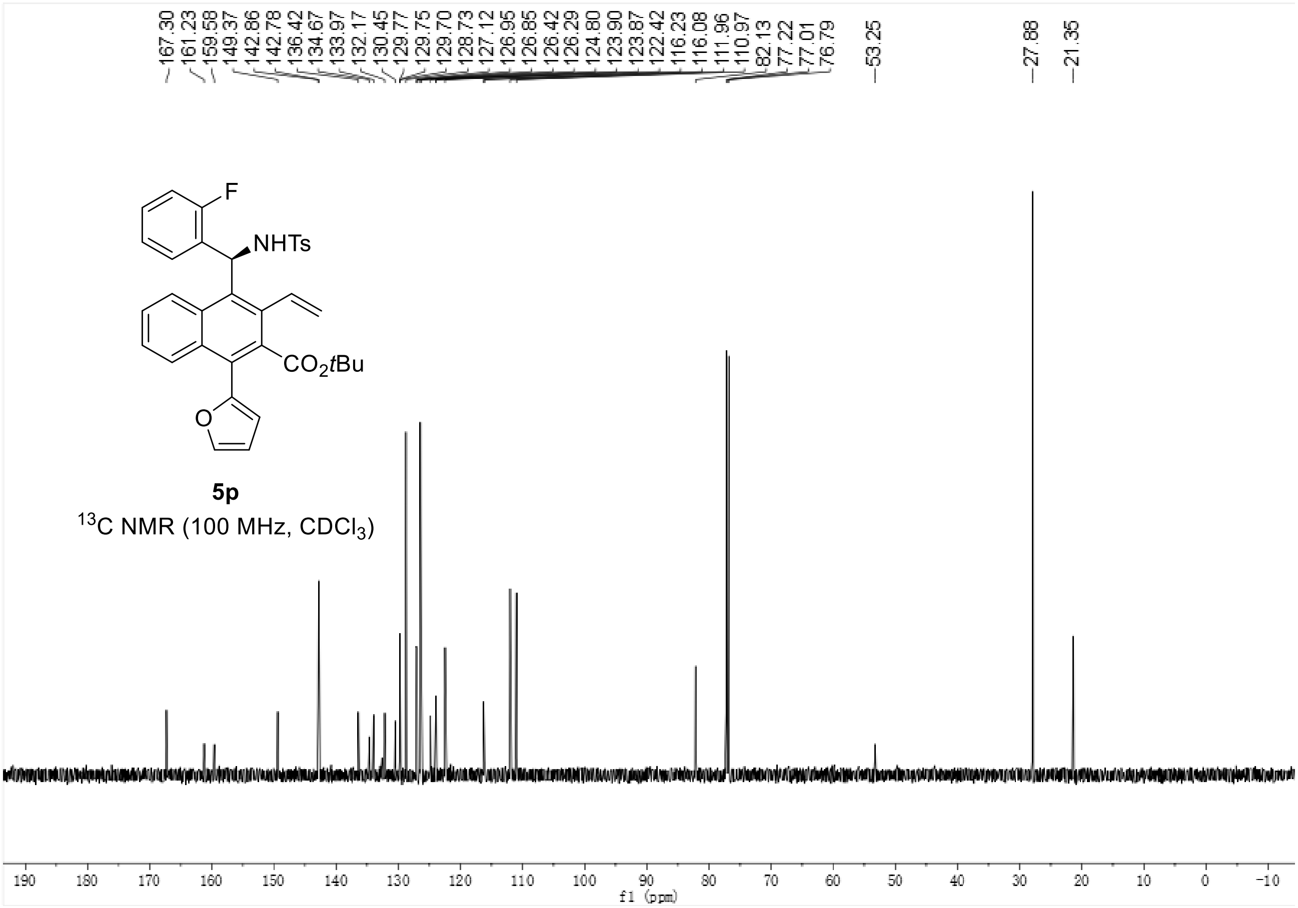


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.229 | BB | 0.23 | 435.7132 | 6695.1084 | 93.0066 |
| 10.403 | BBA | 0.36 | 21.2800 | 503.4248 | 6.9934 |
| | | | Totals: | 7198.5332 | 100.0000 |



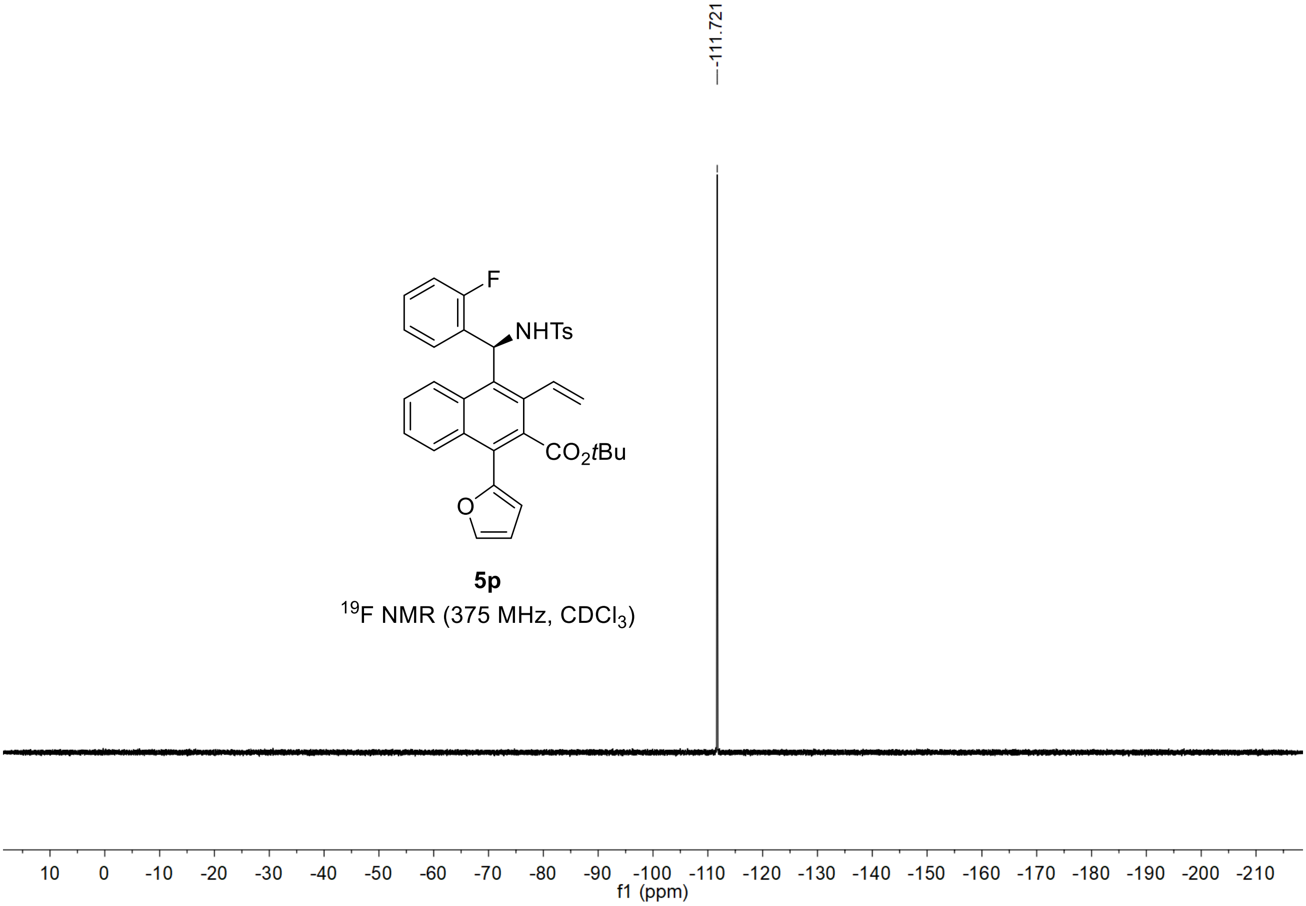
**5p**

$^1$H NMR (400 MHz, CDCl$_3$)



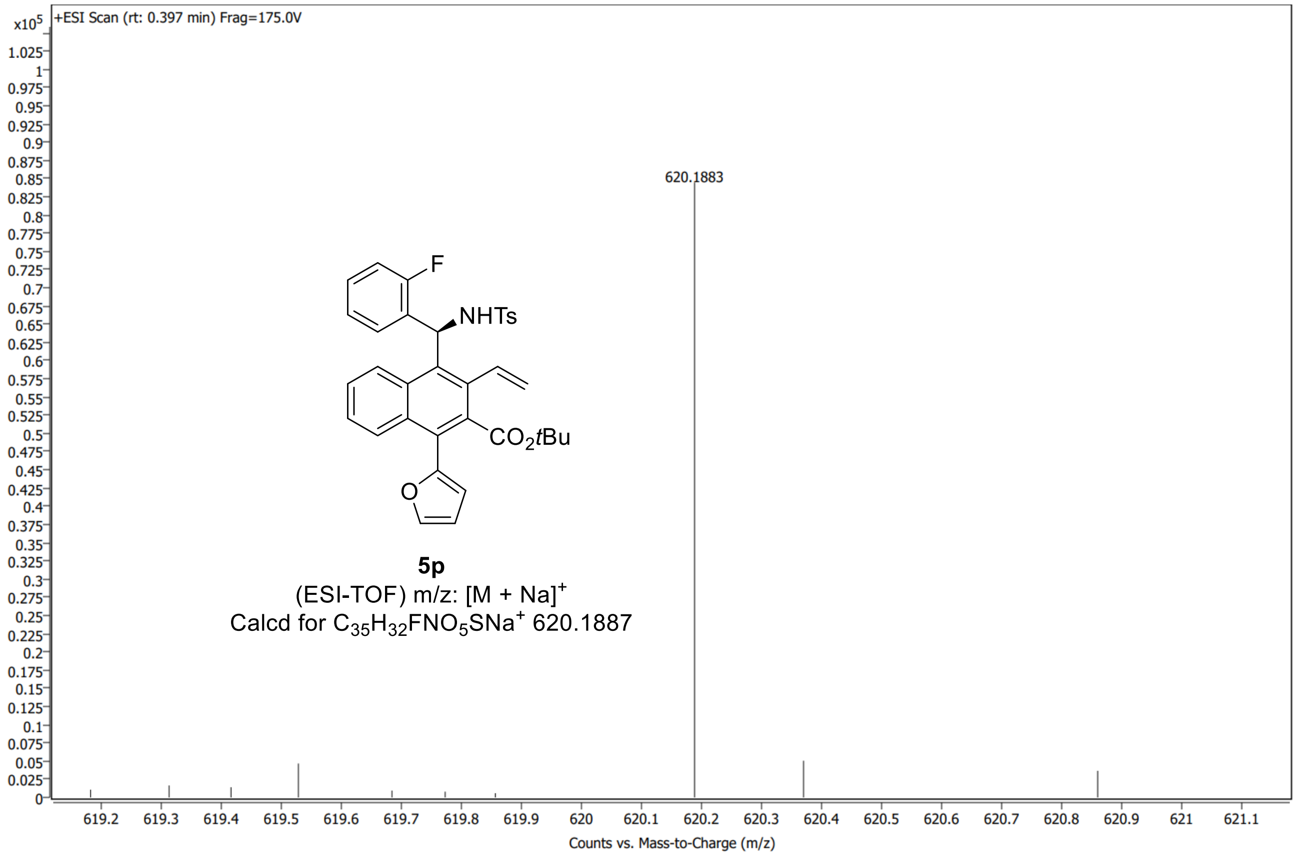
**5p**

$^{13}$C NMR (100 MHz, CDCl$_3$)



**5p**

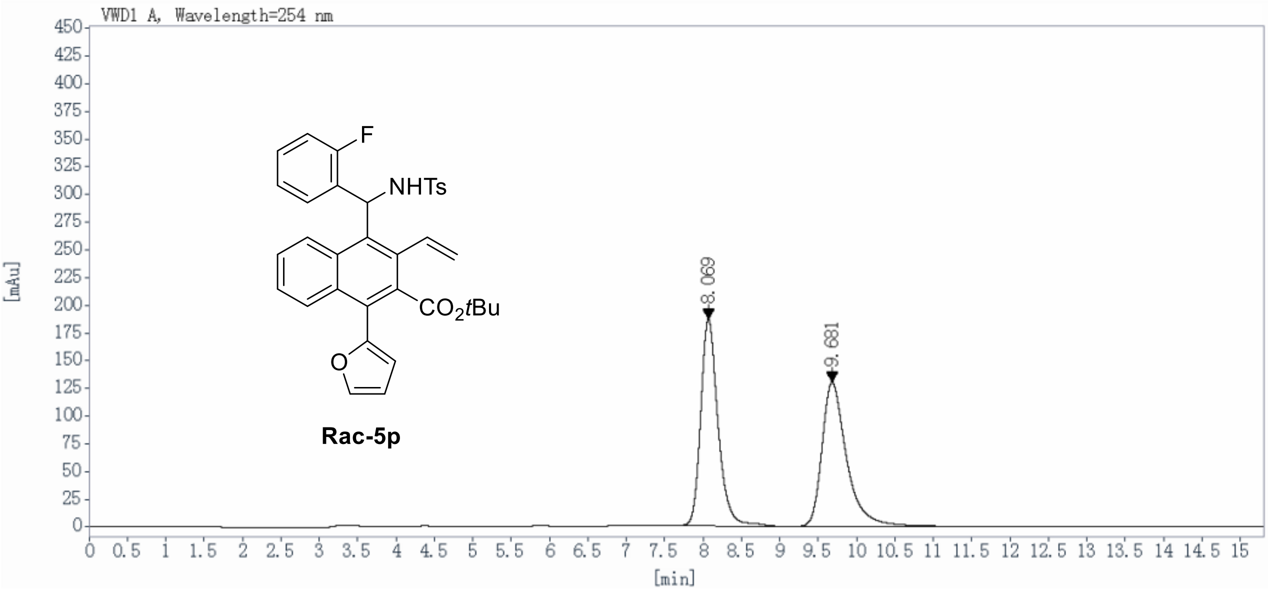
$^{19}$F NMR (375 MHz, CDCl$_3$)



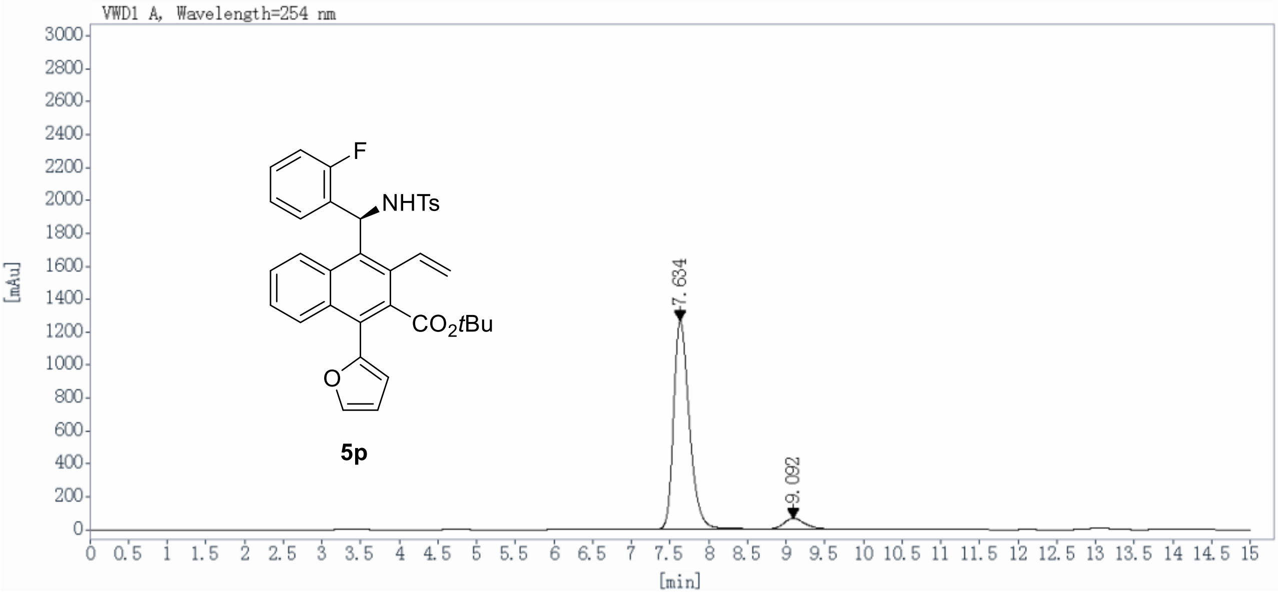
**5p**

(ESI-TOF) m/z: [M + Na]$^+$

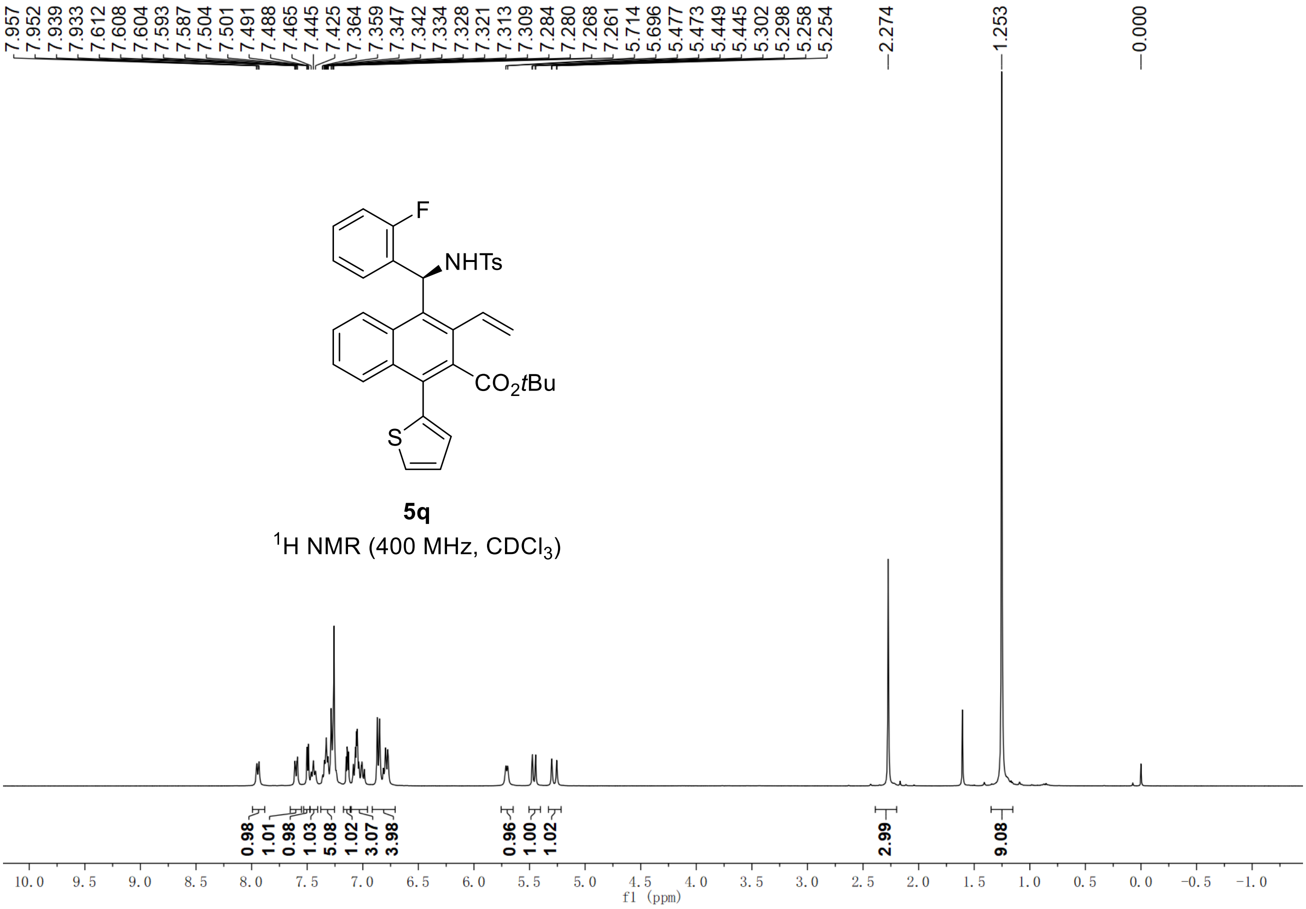
Calcd for $C_{35}H_{32}FNO_5SNa^+$ 620.1887

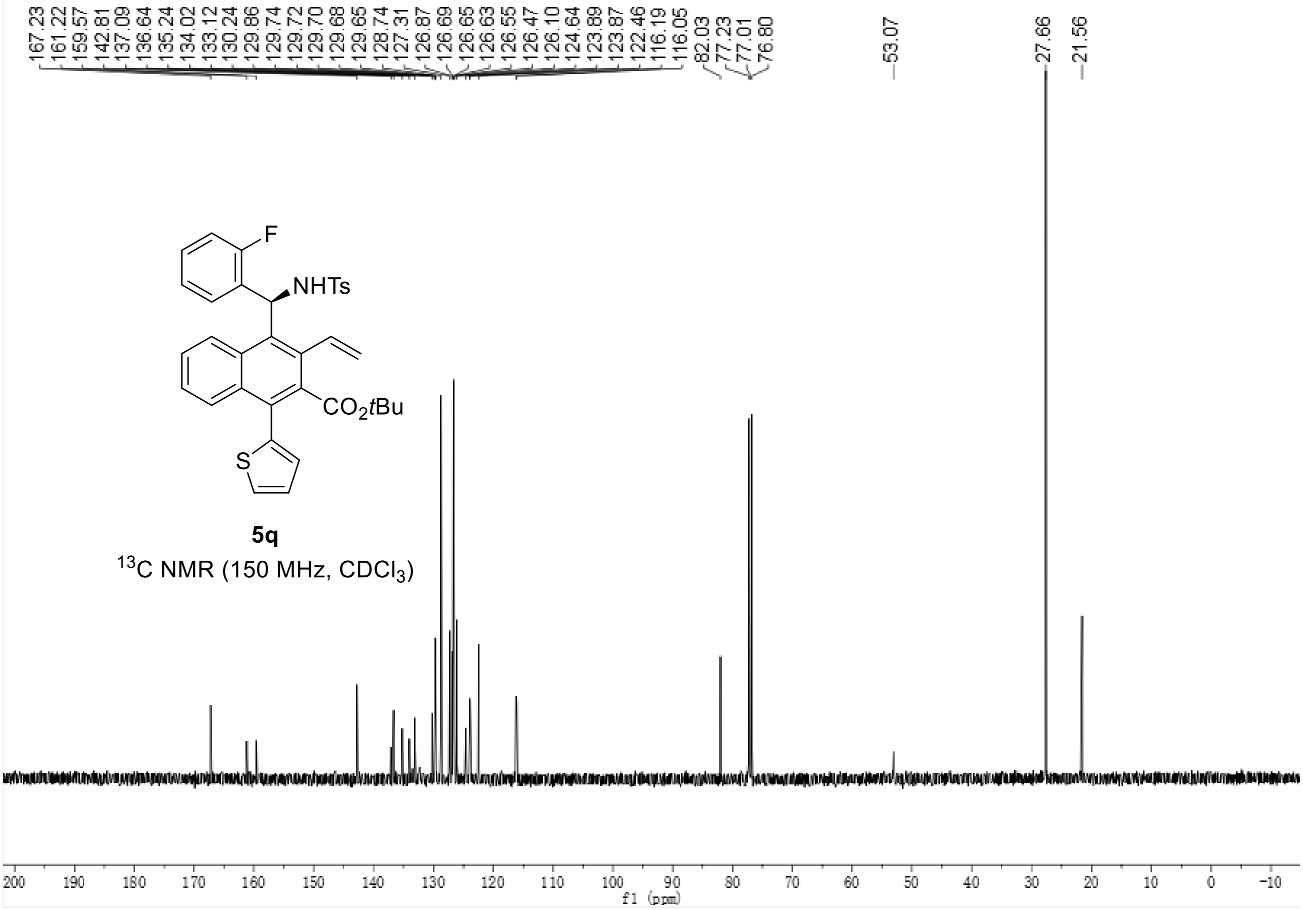


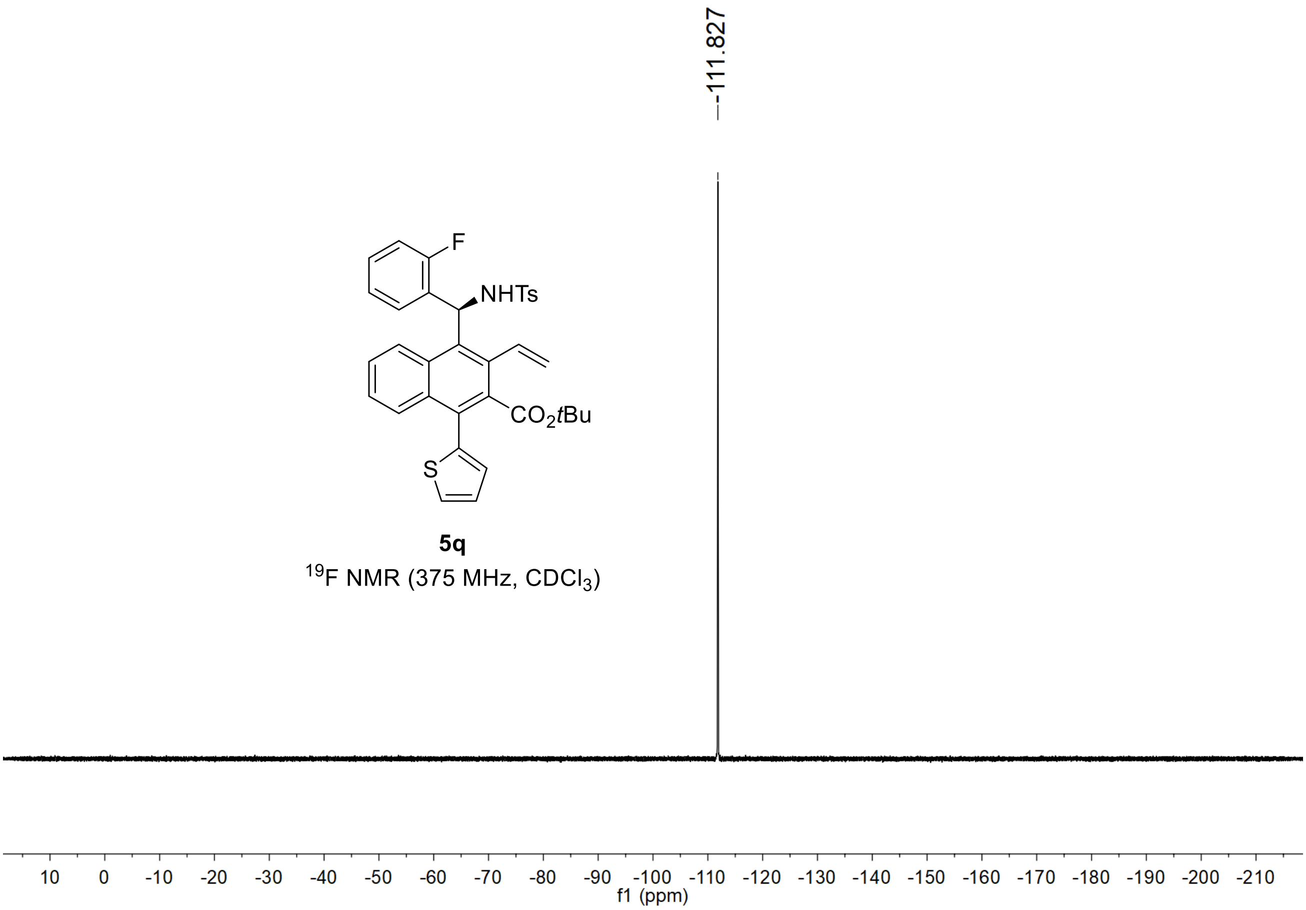
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.069 | VBAR | 0.24 | 186.6031 | 2945.9395 | 50.2008 |
| 9.681 | BB | 0.34 | 130.3542 | 2922.3713 | 49.7992 |
|  |  |  | Totals: | 5868.3108 | 100.0000 |



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.634 | VBAR | 0.22 | 1268.8865 | 18013.0625 | 93.8242 |
| 9.092 | BBA | 0.28 | 64.8426 | 1185.6801 | 6.1758 |
|  |  |  | Totals: | 19198.7426 | 100.0000 |

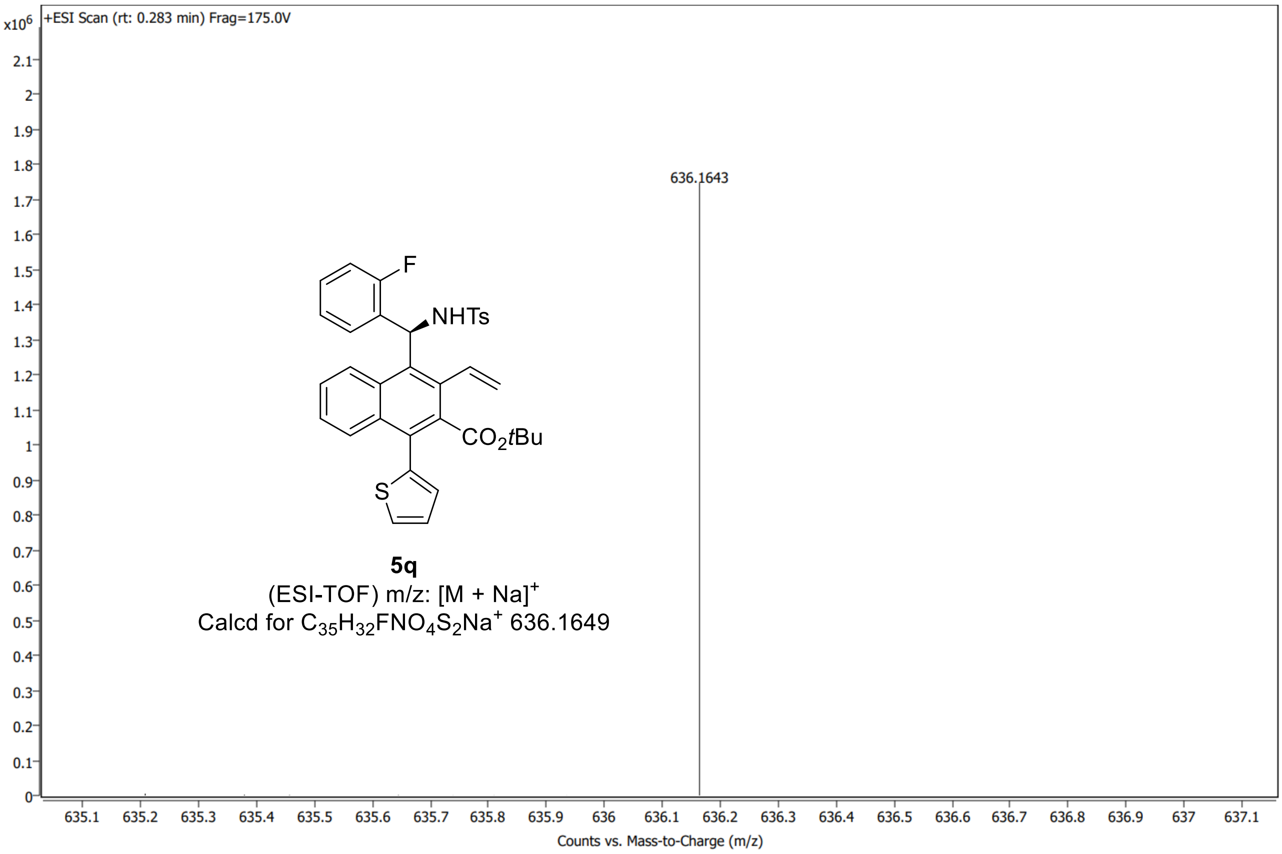

7.957
7.952
7.939
7.933
7.612
7.608
7.604
7.593
7.587
7.504
7.501
7.491
7.488
7.465
7.445
7.425
7.364
7.359
7.347
7.342
7.334
7.328
7.321
7.313
7.309
7.284
7.280
7.268
7.261
5.714
5.696
5.477
5.473
5.449
5.445
5.302
5.298
5.258
5.254
2.274
1.253
0.000
F
NHTs
CO2tBu
S
5q
1H NMR (400 MHz, CDCl3)
0.98
1.01
0.98
1.03
5.08
1.02
3.07
3.98
0.96
1.00
1.02
2.99
9.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.23
161.22
159.57
142.81
137.09
136.64
135.24
134.02
133.12
130.24
129.86
129.74
129.72
129.70
129.68
129.65
128.74
127.31
126.87
126.69
126.65
126.63
126.55
126.47
126.10
124.64
123.89
123.87
122.46
116.19
116.05
82.03
77.23
77.01
76.80
53.07
27.66
21.56
F
NHTs
CO2tBu
S
5q
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



**5q**

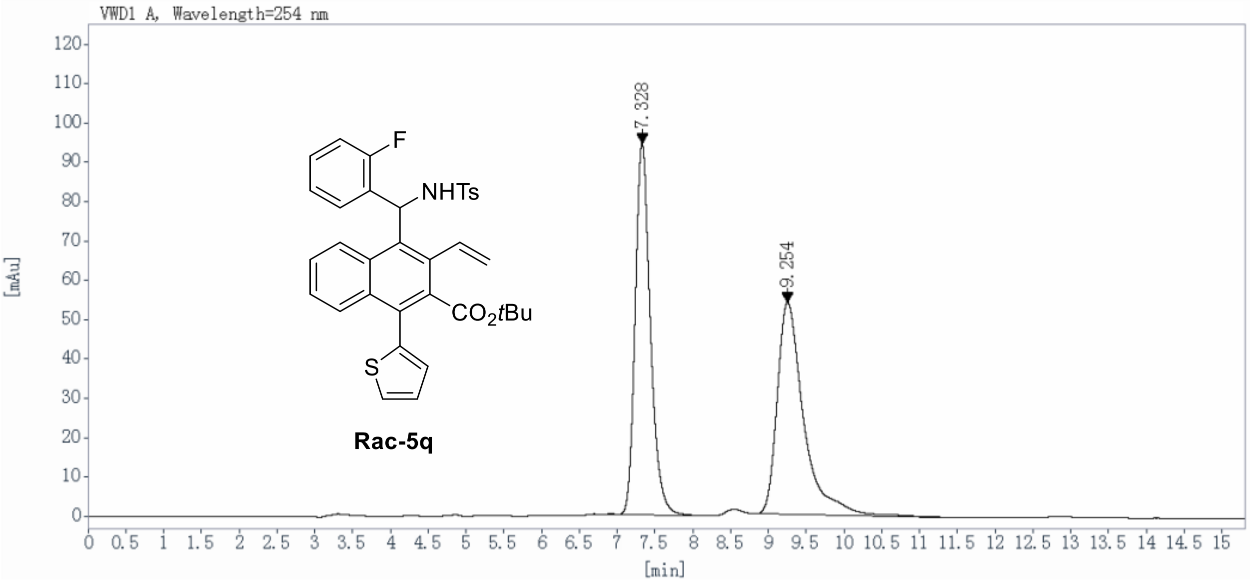
$^{19}$F NMR (375 MHz, CDCl$_3$)



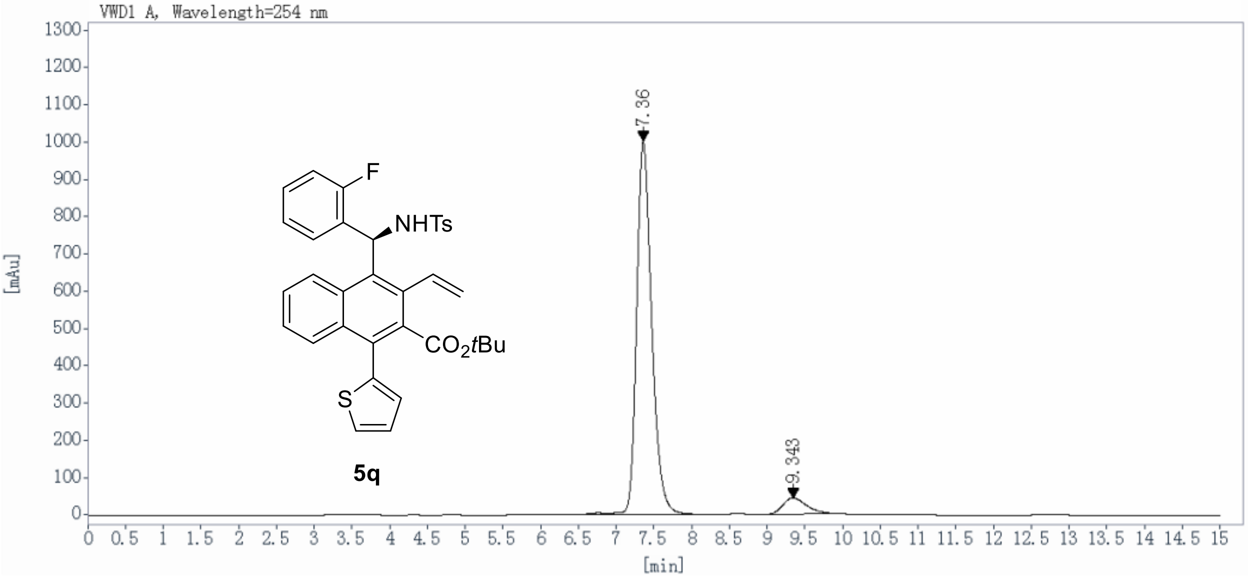
**5q**

(ESI-TOF) m/z: [M + Na]$^+$

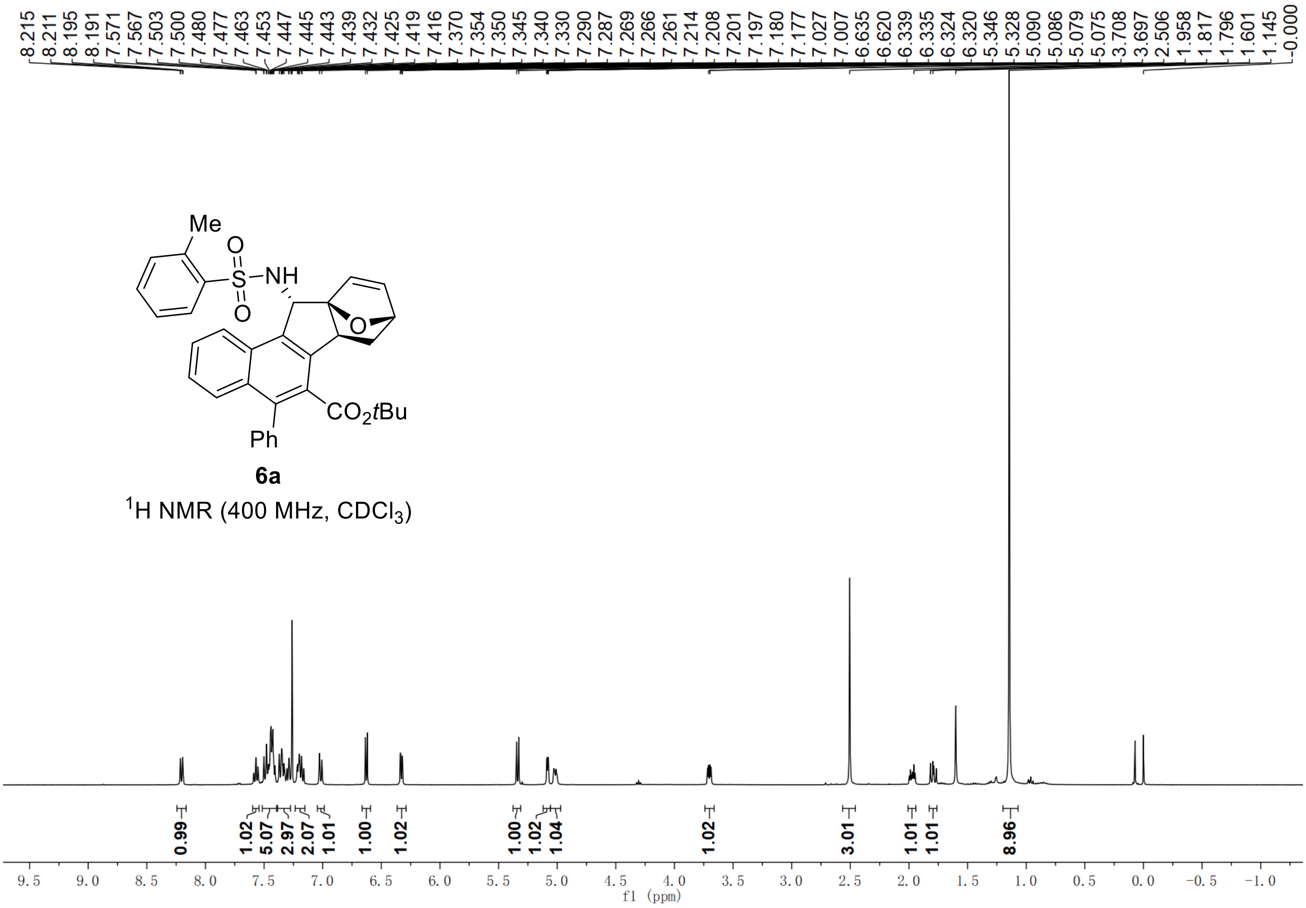
Calcd for $C_{35}H_{32}FNO_4S_2Na^+$ 636.1649



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.328 | VBAR | 0.21 | 94.5603 | 1330.9934 | 50.3355 |
| 9.254 | BB | 0.36 | 53.9834 | 1313.2479 | 49.6645 |
| | | | Totals: | 2644.2413 | 100.0000 |

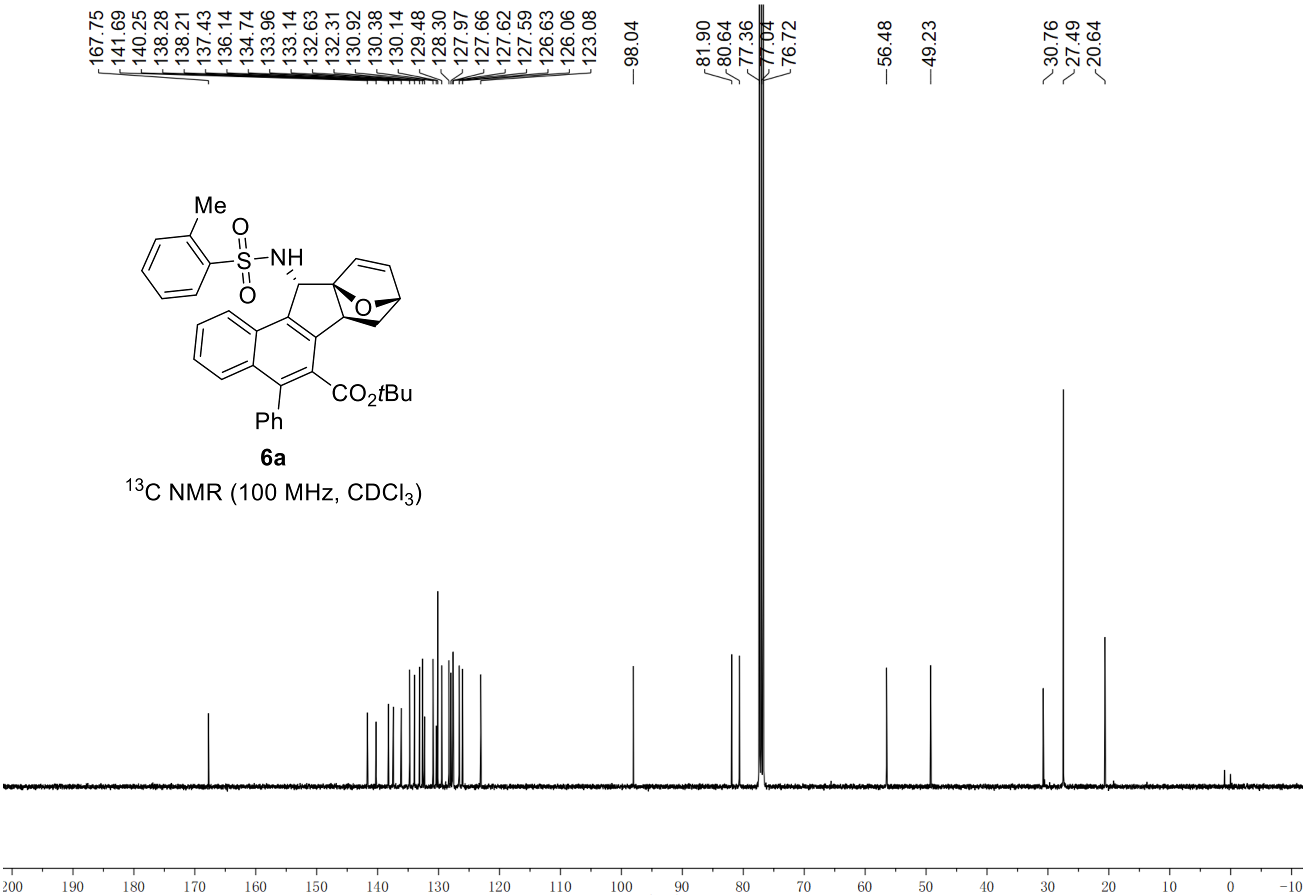


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.360 | VBAR | 0.22 | 1001.2925 | 14140.5576 | 93.4809 |
| 9.343 | BBA | 0.34 | 44.1863 | 986.1213 | 6.5191 |
| | | | Totals: | 15126.6790 | 100.0000 |



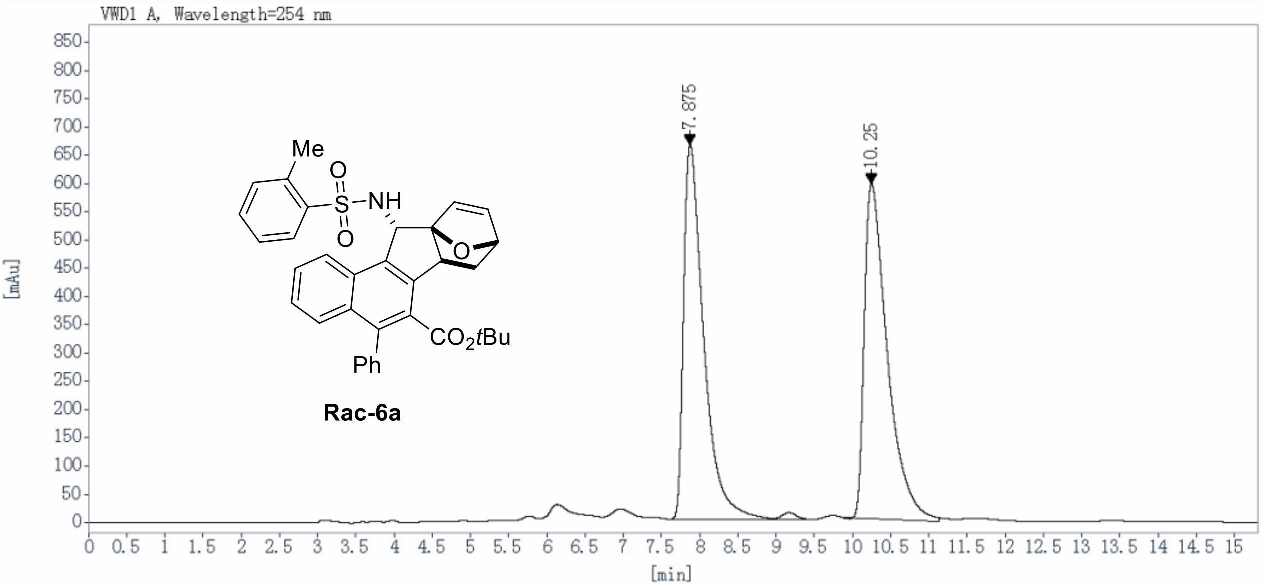
**6a**

$^1$H NMR (400 MHz, CDCl$_3$)

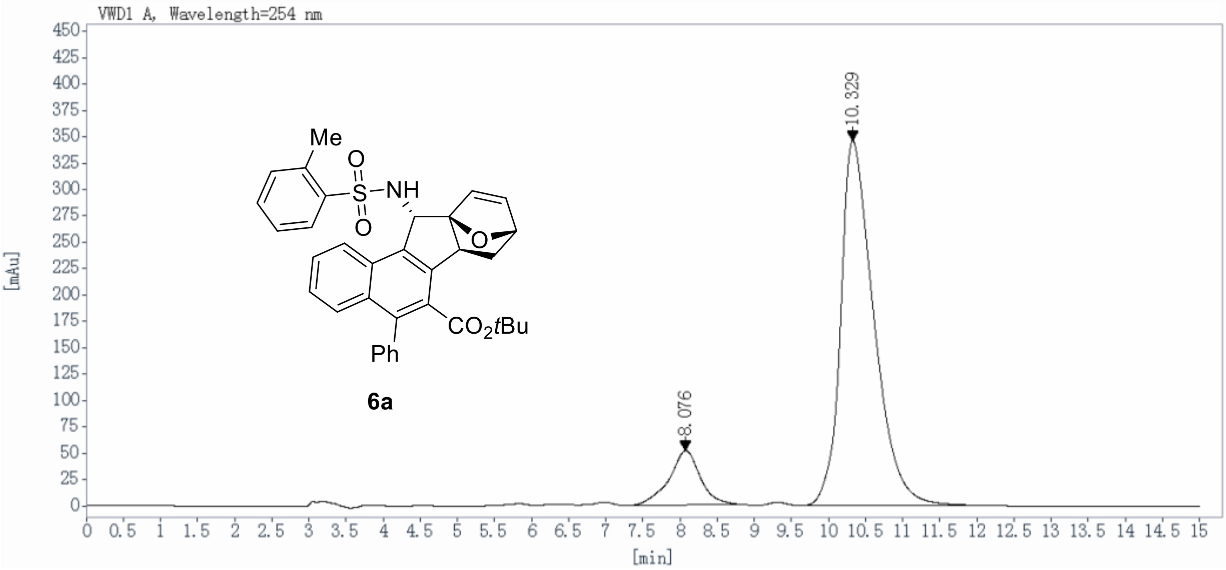


**6a**

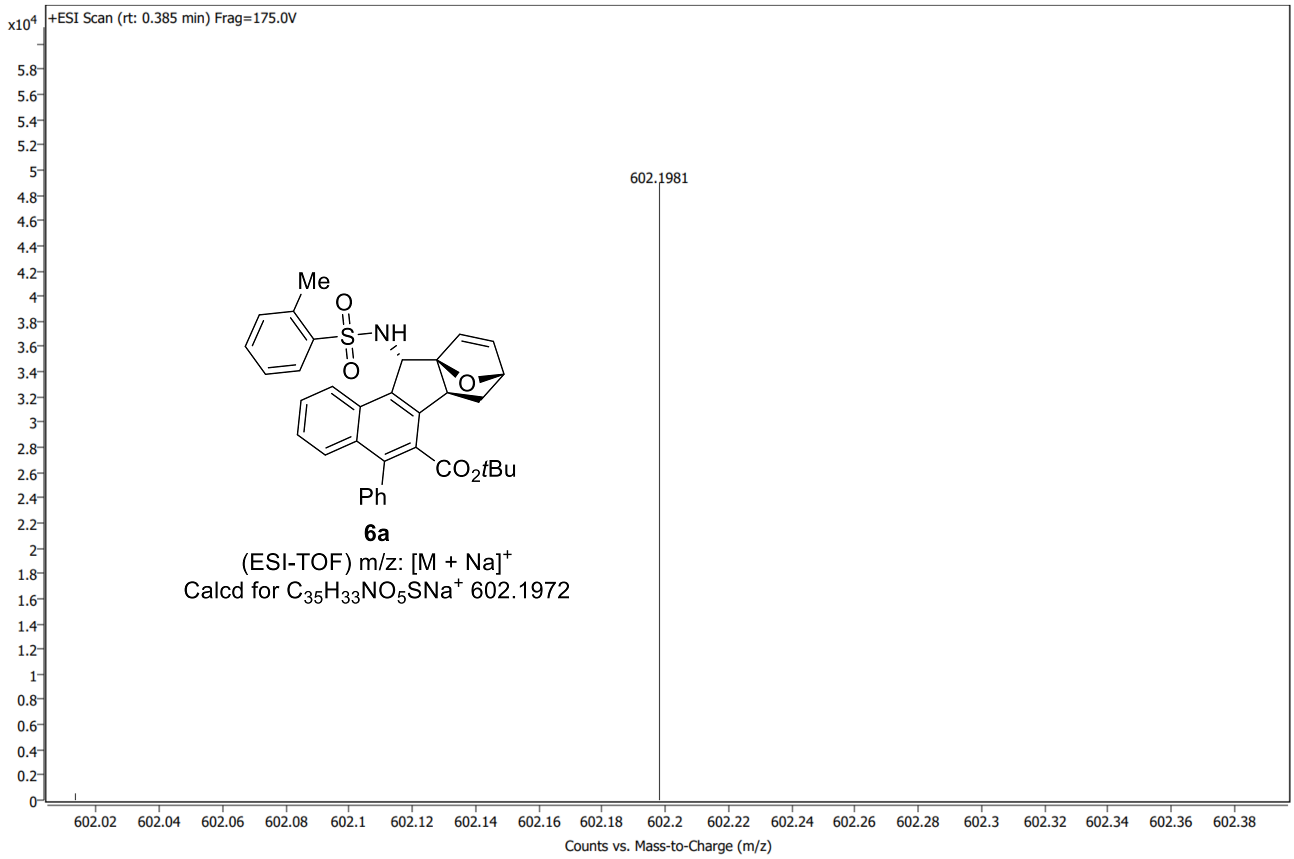
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.875 | BV R | 0.28 | 663.1407 | 12343.9590 | 49.8141 |
| 10.250 | MM | 0.35 | 592.7851 | 12436.1064 | 50.1859 |
|  |  |  | Totals: | 24780.0654 | 100.0000 |



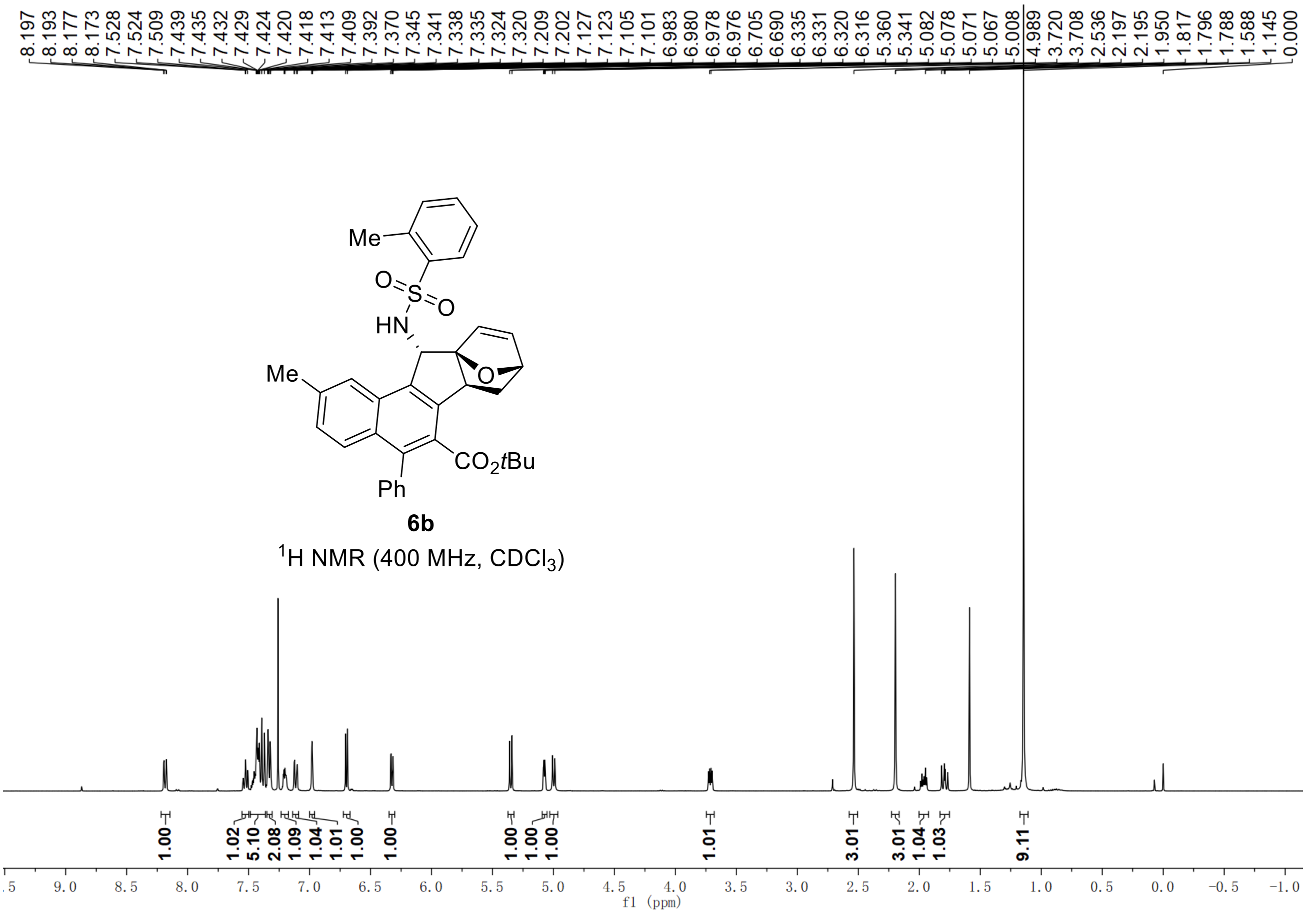
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.076 | BBA | 0.43 | 51.5447 | 1530.3451 | 12.4035 |
| 10.329 | BBA | 0.47 | 345.7148 | 10807.6768 | 87.5965 |
|  |  |  | Totals: | 12338.0219 | 100.0000 |



**6a**

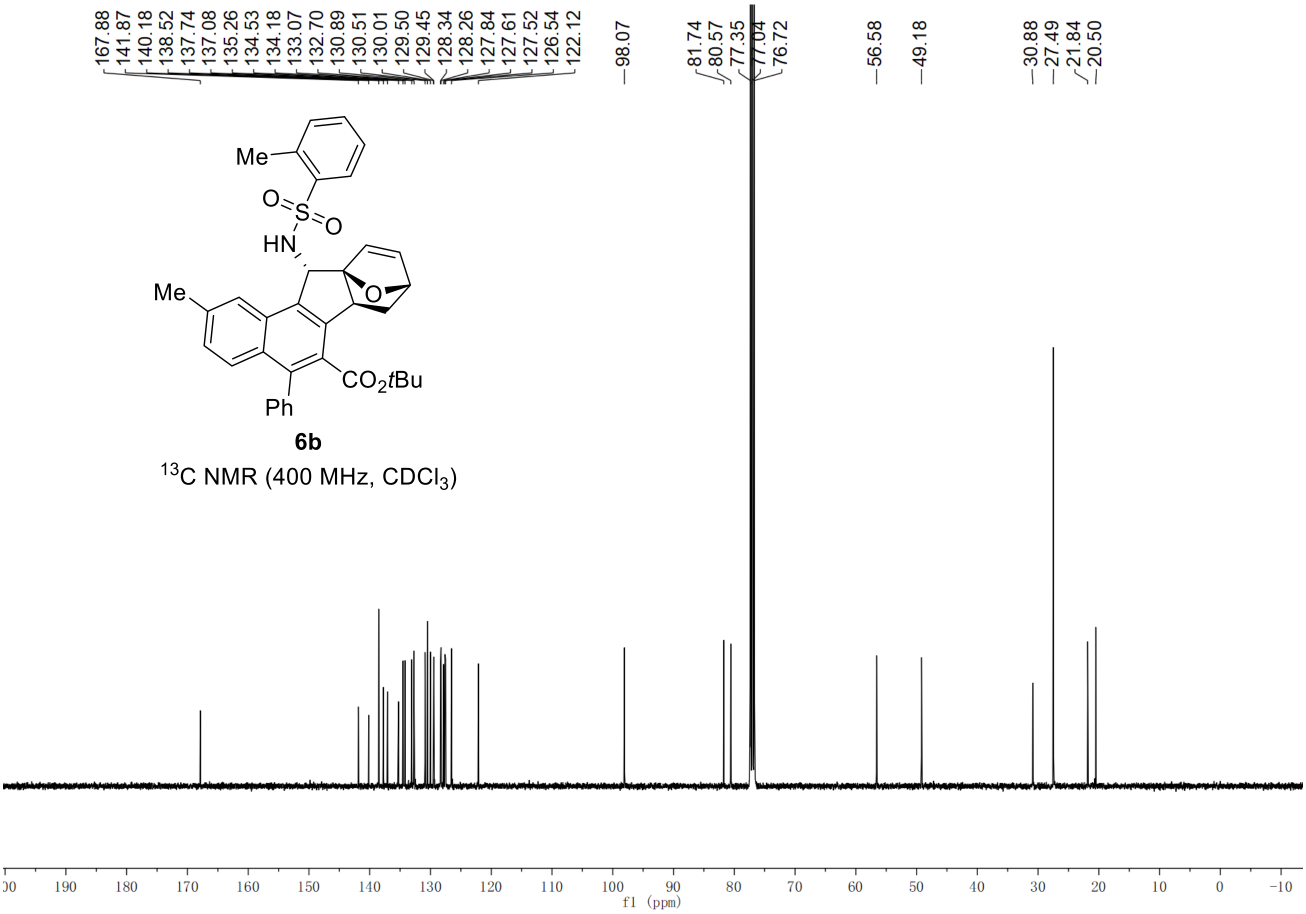
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{35}H_{33}NO_5SNa^+$ 602.1972



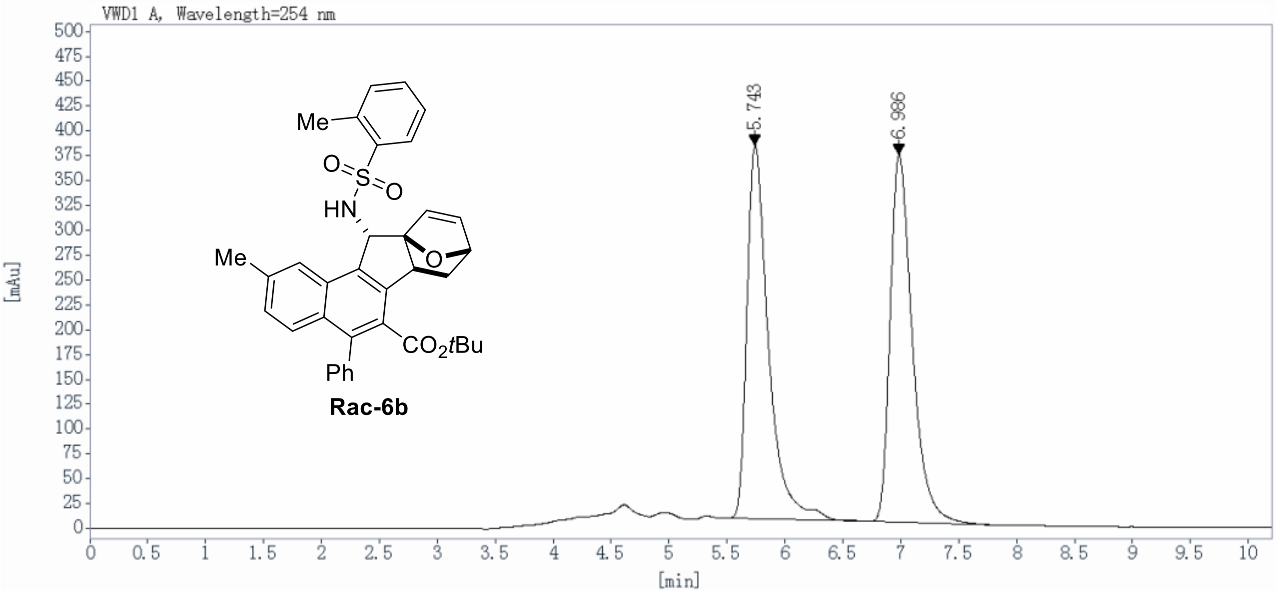
**6b**

$^1$H NMR (400 MHz, CDCl$_3$)



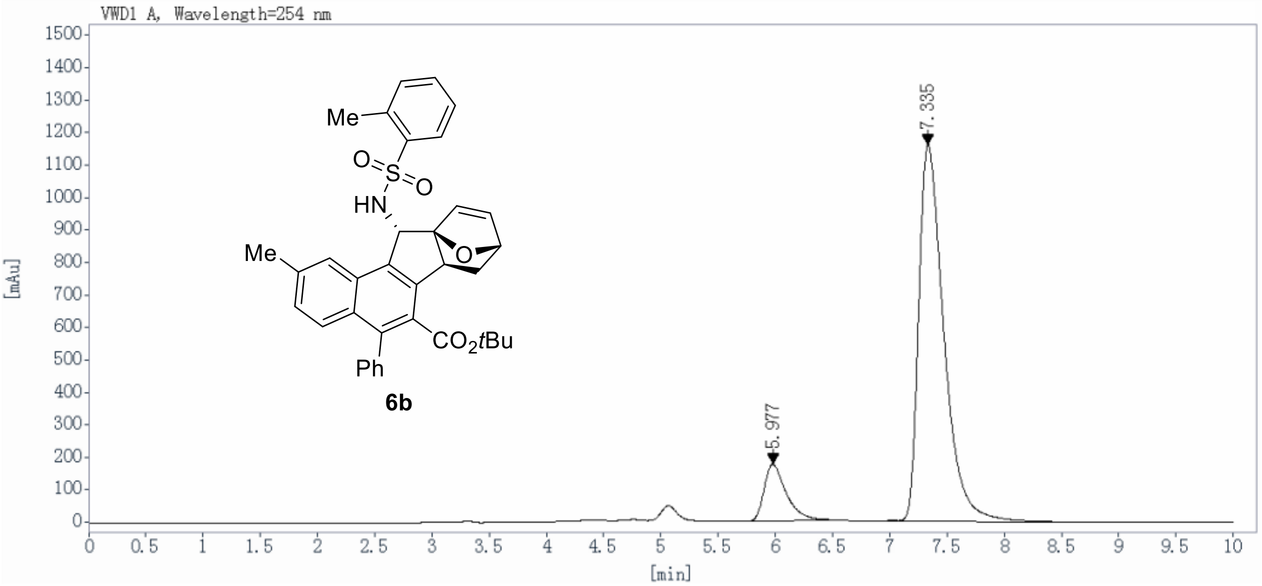
**6b**

$^{13}$C NMR (400 MHz, CDCl$_3$)



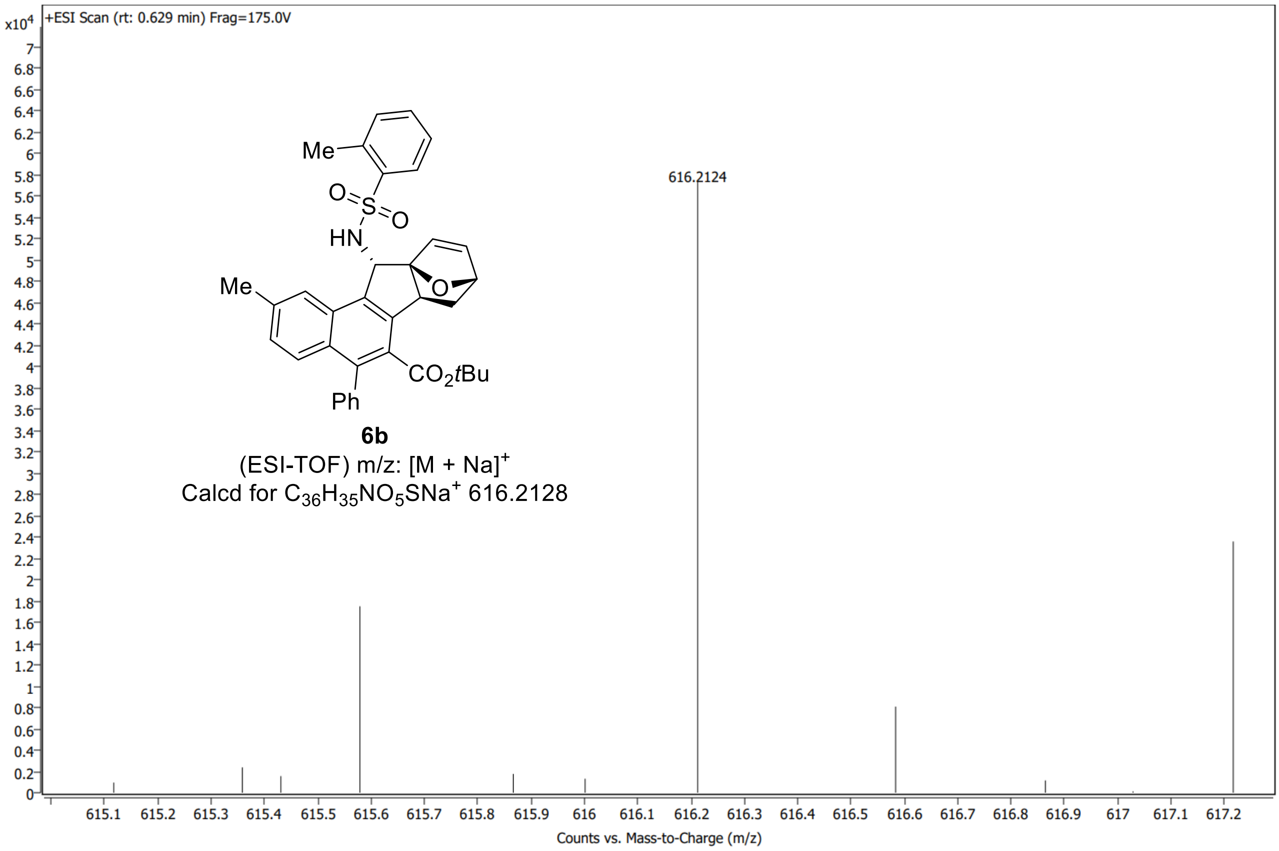
**Rac-6b**

| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.743 | BV R | 0.19 | 376.4645 | 4880.0991 | 49.7970 |
| 6.986 | BB | 0.20 | 369.9242 | 4919.8867 | 50.2030 |
| | | | Totals: | 9799.9858 | 100.0000 |



**6b**

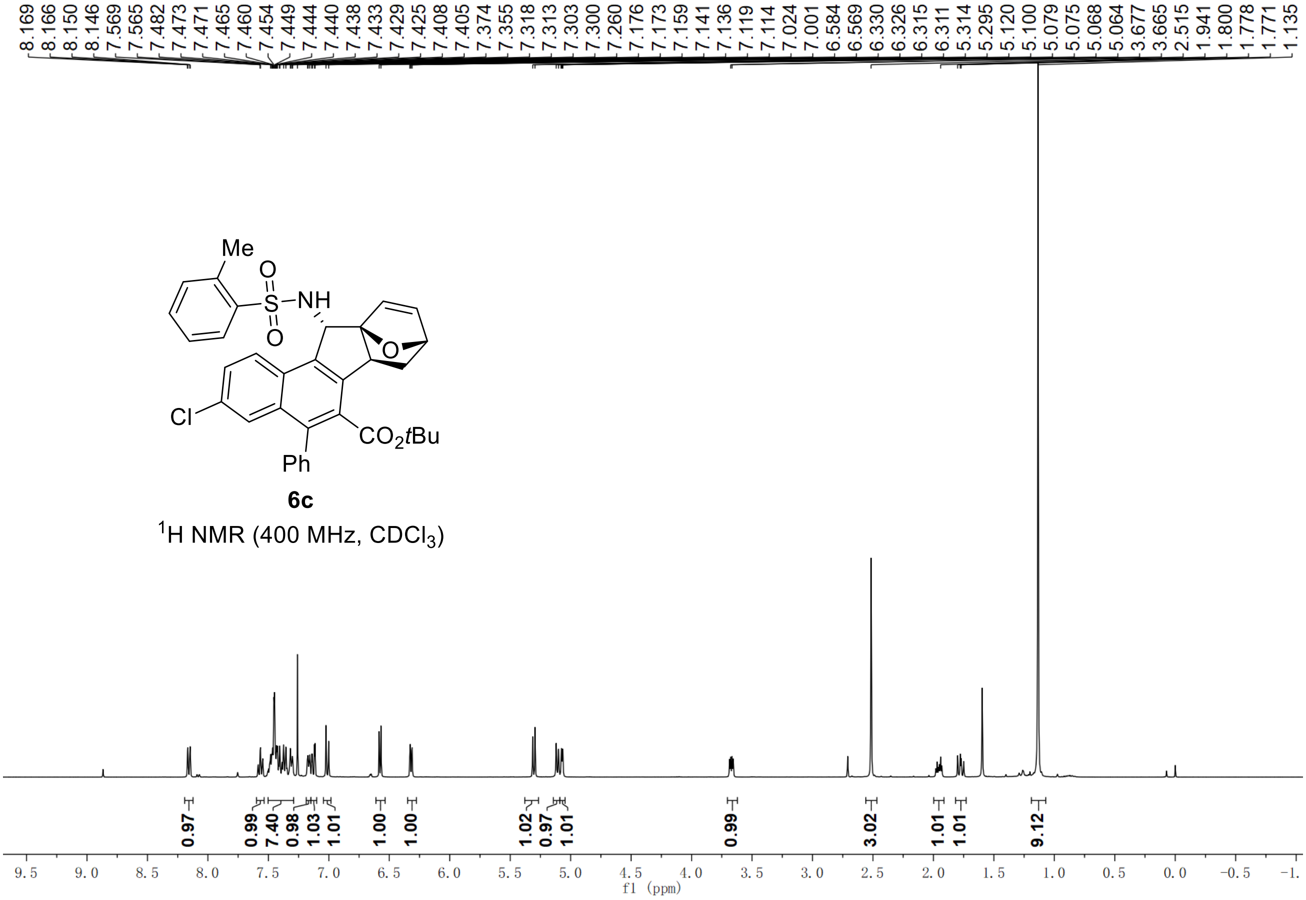
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.977 | BBA | 0.20 | 175.5388 | 2383.9958 | 11.7948 |
| 7.335 | VBAR | 0.23 | 1161.0538 | 17828.3496 | 88.2052 |
| | | | Totals: | 20212.3455 | 100.0000 |



**6b**

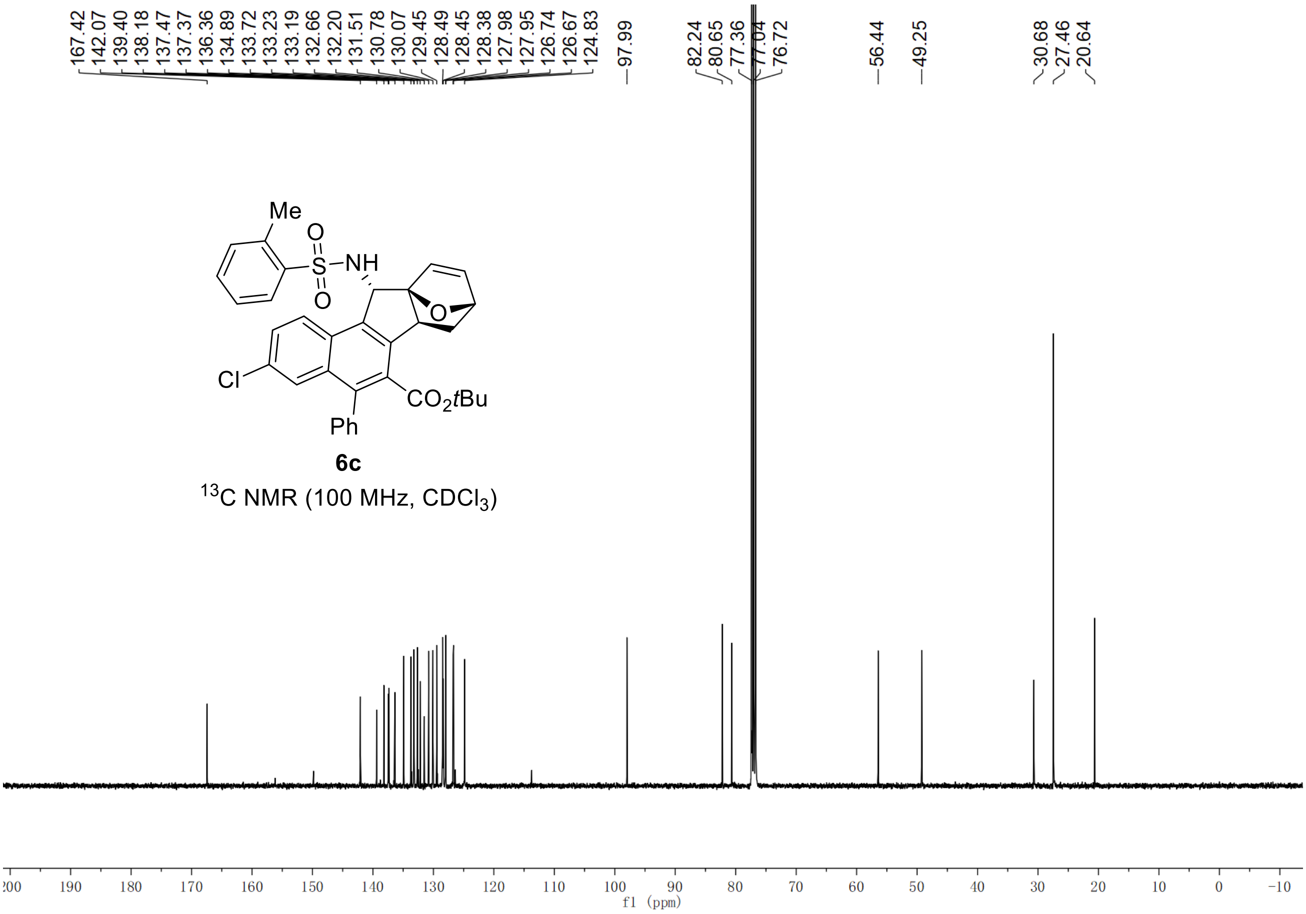
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{36}H_{35}NO_5SNa^+$ 616.2128



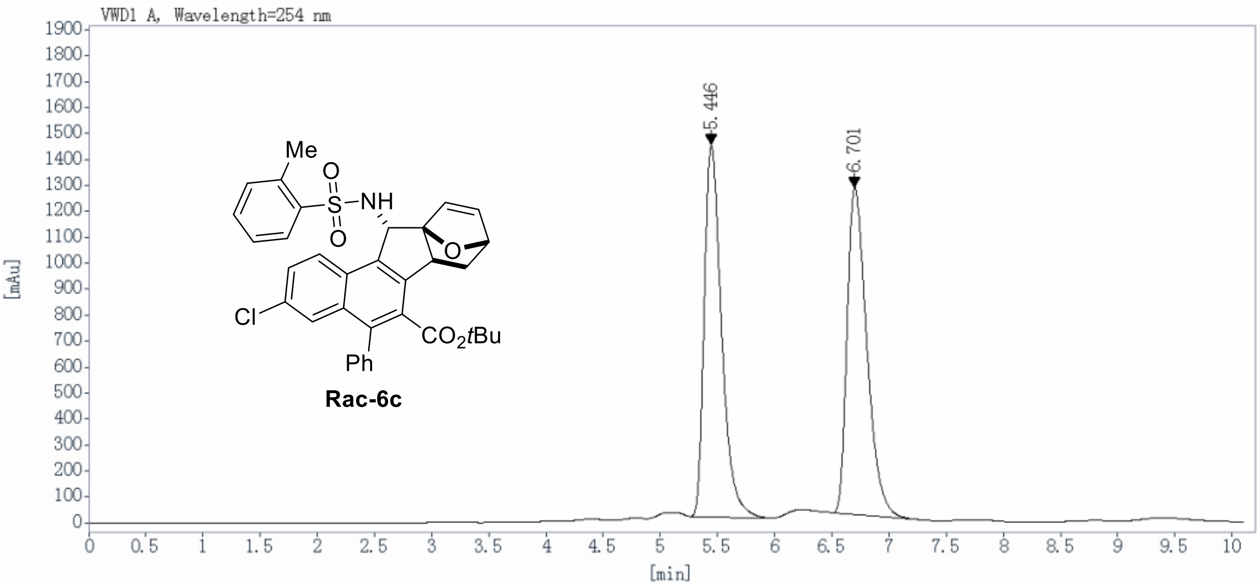
**6c**

$^{1}$H NMR (400 MHz, $CDCl_3$)

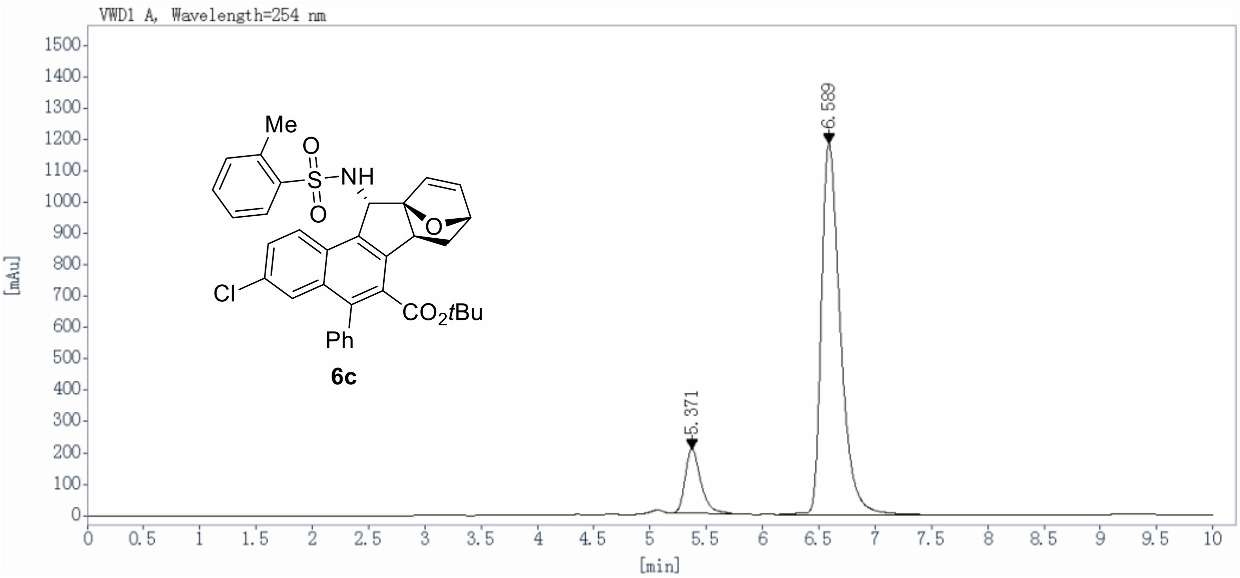


**6c**

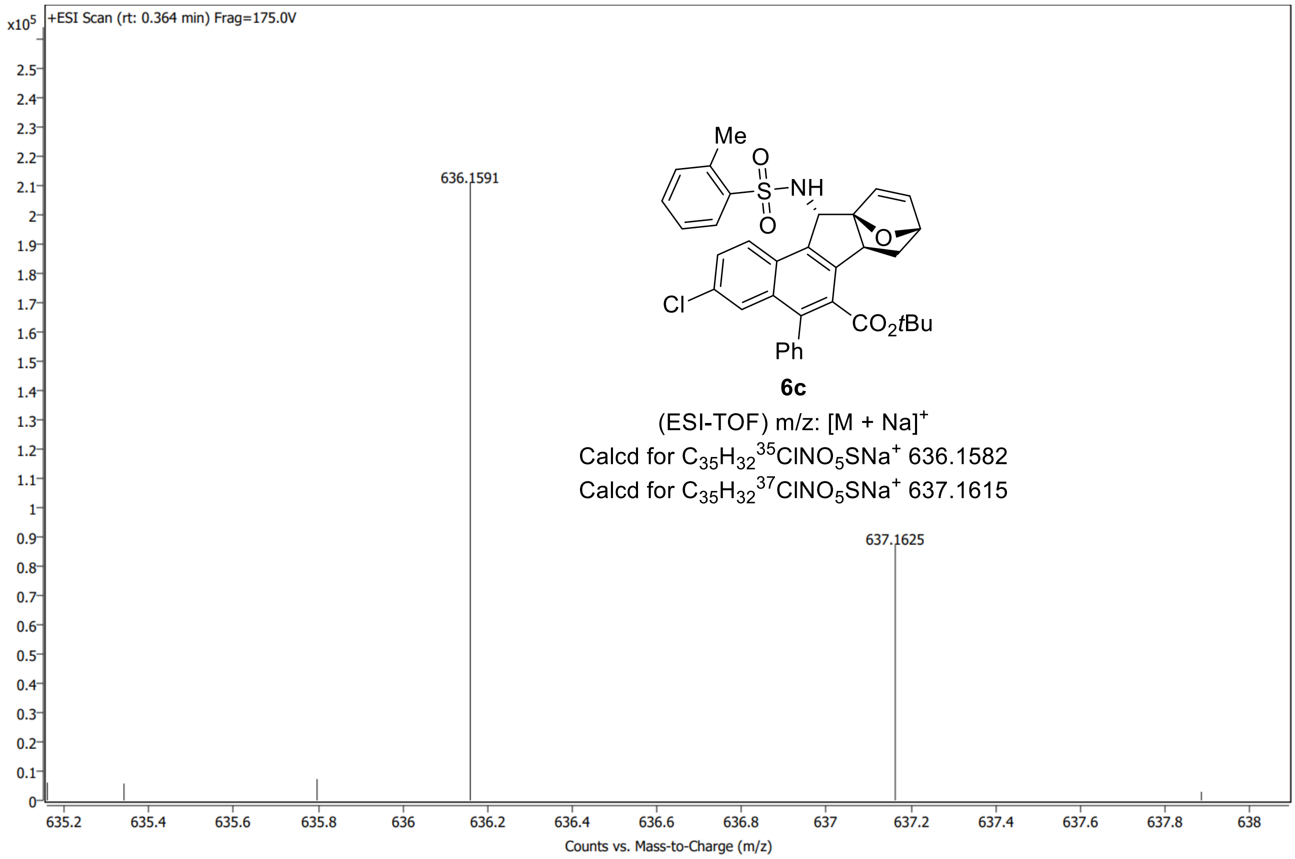
$^{13}$C NMR (100 MHz, $CDCl_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.446 | BBA | 0.16 | 1434.5337 | 15108.5186 | 49.9358 |
| 6.701 | BBA | 0.19 | 1261.0889 | 15147.3936 | 50.0642 |
| | | | Totals: | 30255.9121 | 100.0000 |



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 5.371 | BB | 0.15 | 206.4075 | 2019.1595 | 12.7252 |
| 6.589 | VB R | 0.18 | 1183.7113 | 13848.3047 | 87.2748 |
| | | | Totals: | 15867.4642 | 100.0000 |

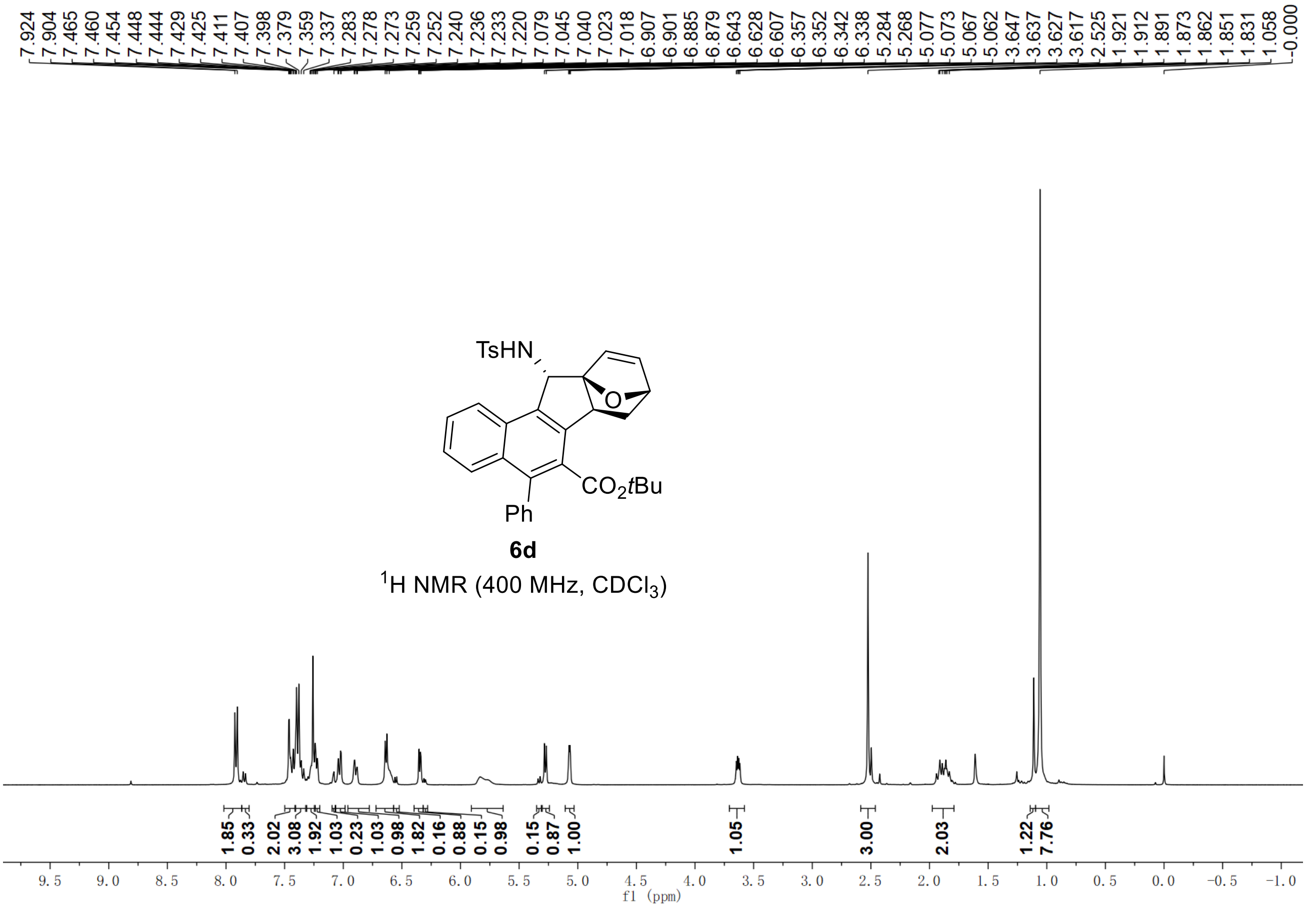


**6c**

(ESI-TOF) m/z: $[M + Na]^+$

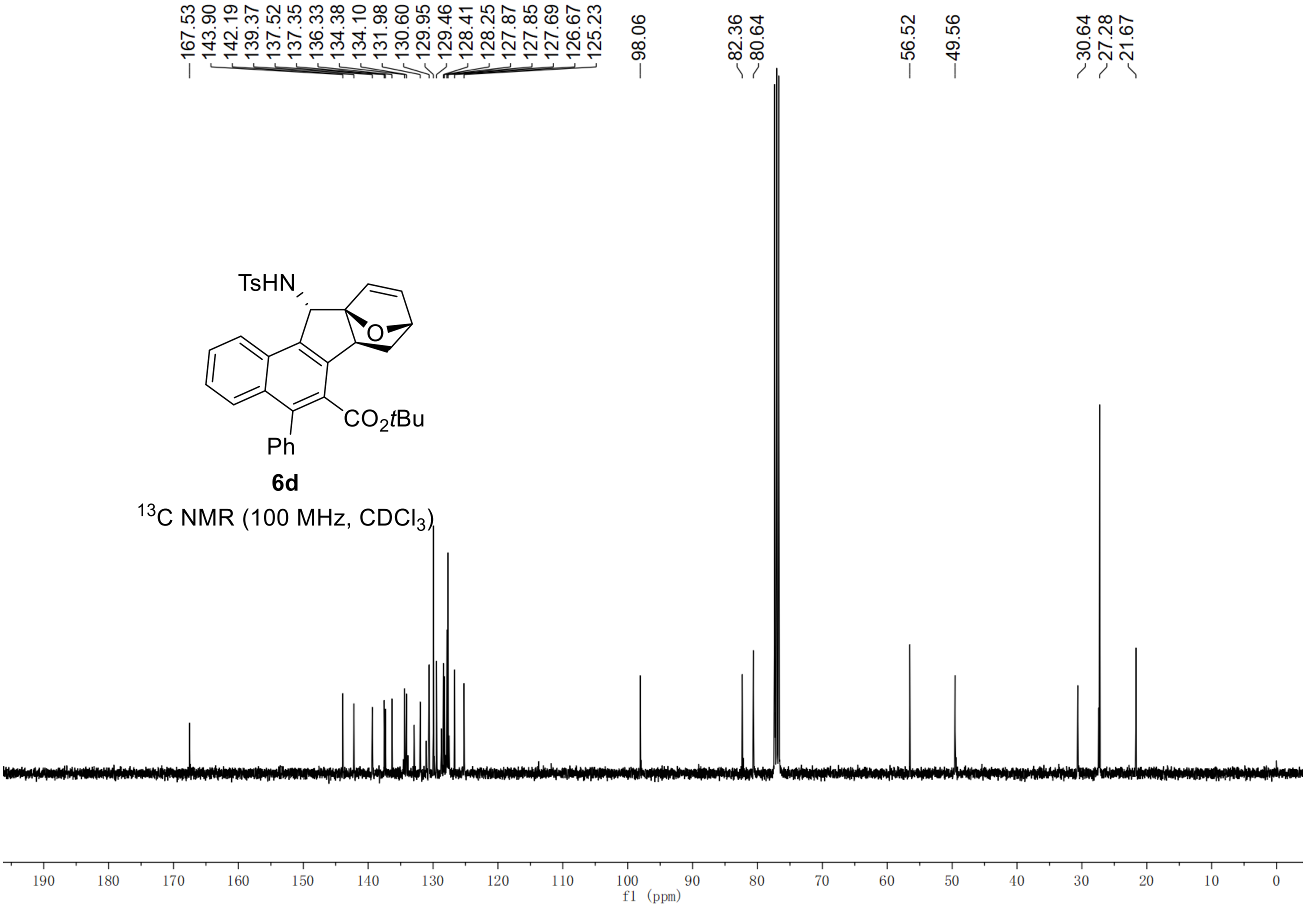
Calcd for $C_{35}H_{32}{}^{35}ClNO_5SNa^+$ 636.1582

Calcd for $C_{35}H_{32}{}^{37}ClNO_5SNa^+$ 637.1615



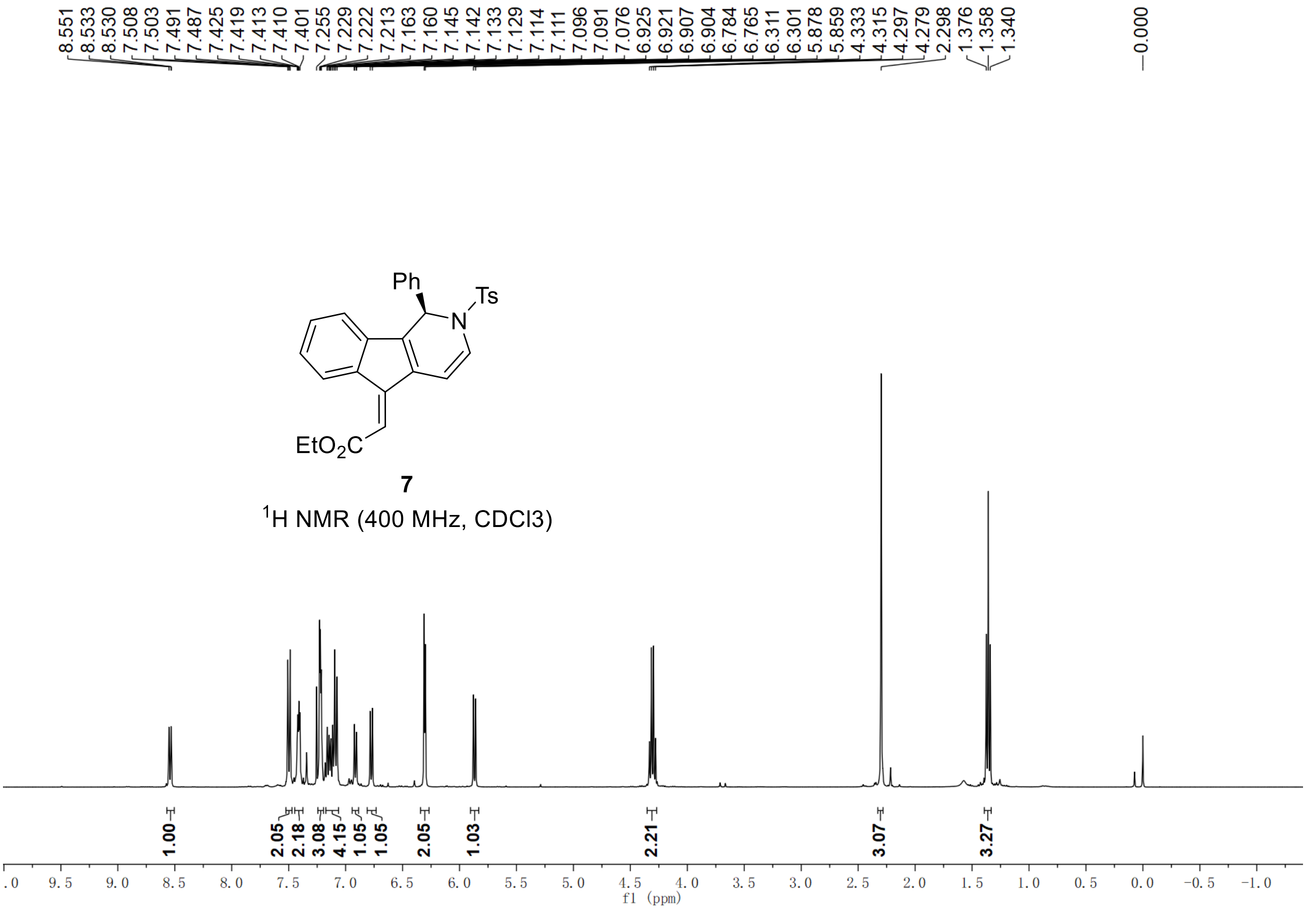
**6d**

$^1$H NMR (400 MHz, CDCl$_3$)



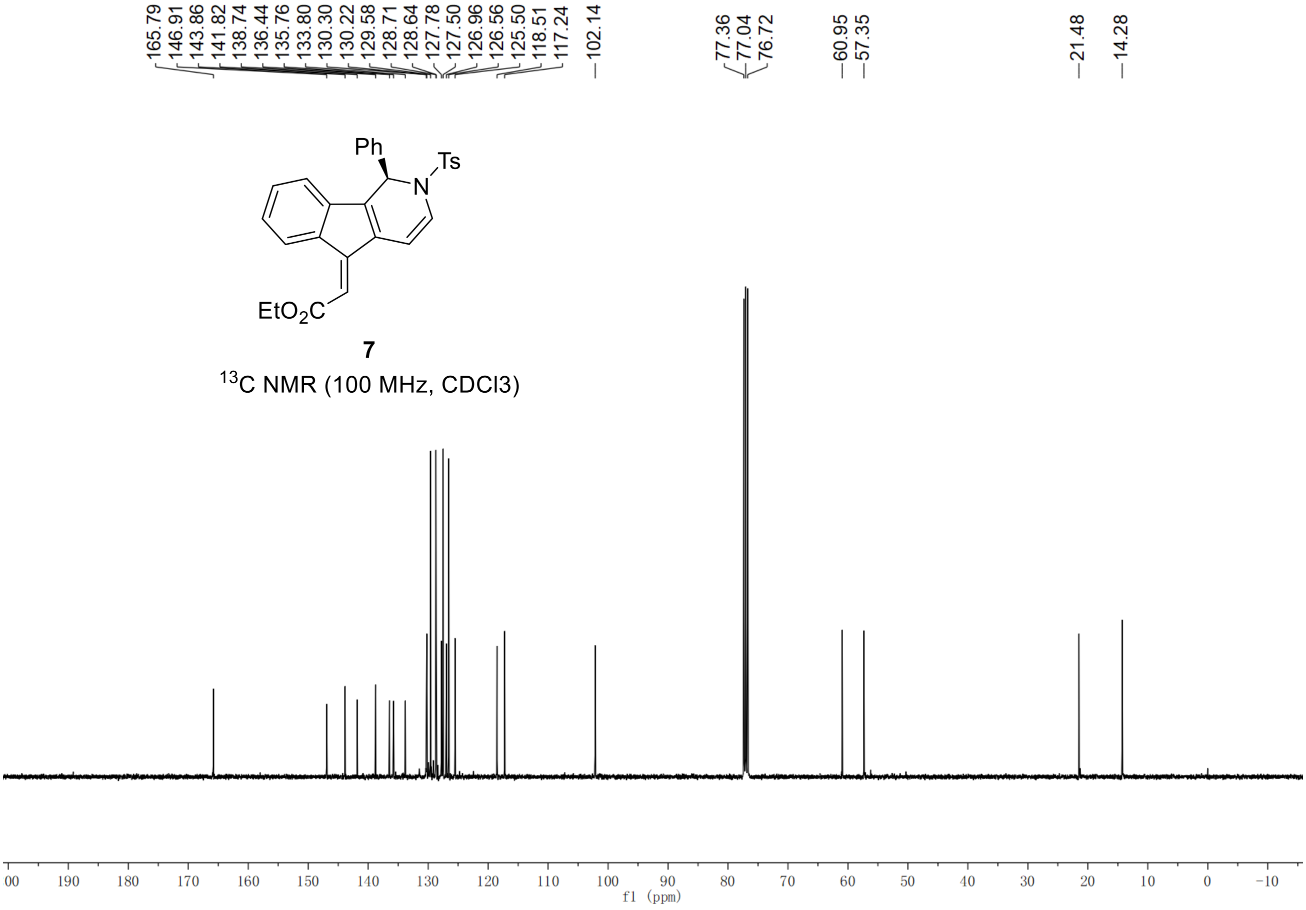
**6d**

$^{13}$C NMR (100 MHz, CDCl$_3$)



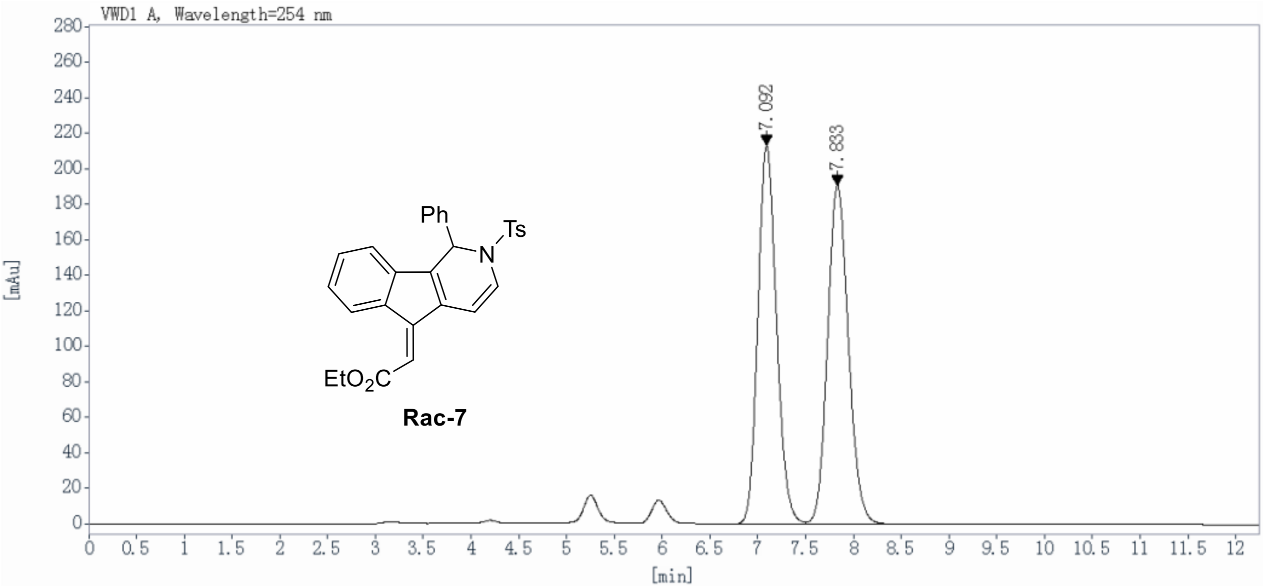
**7**

$^1$H NMR (400 MHz, CDCl3)

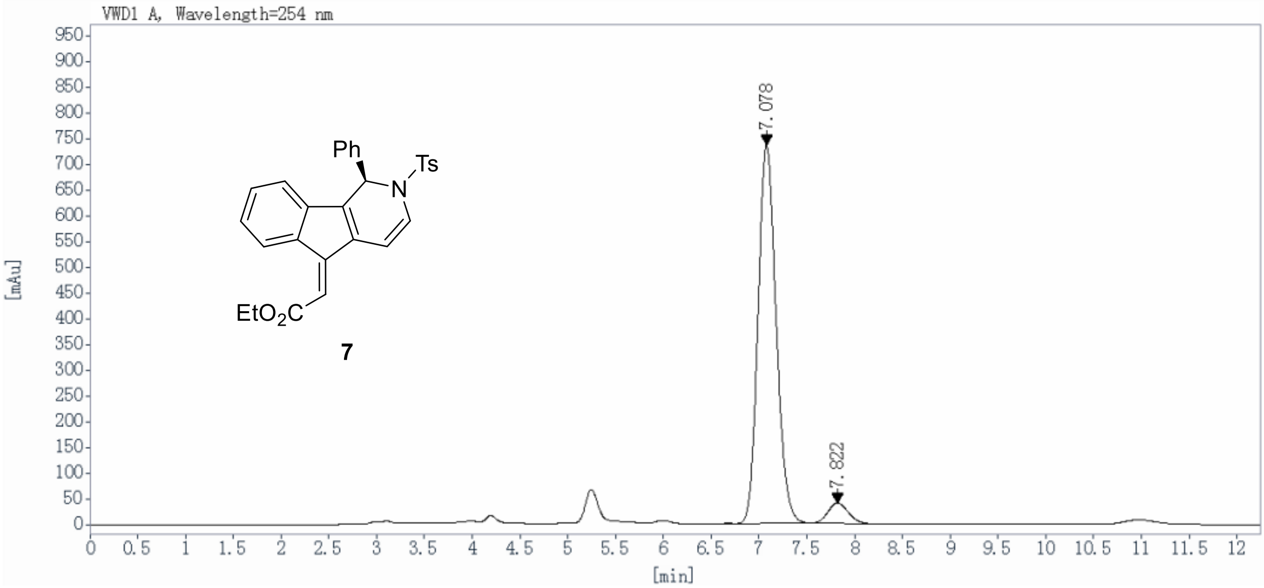


**7**

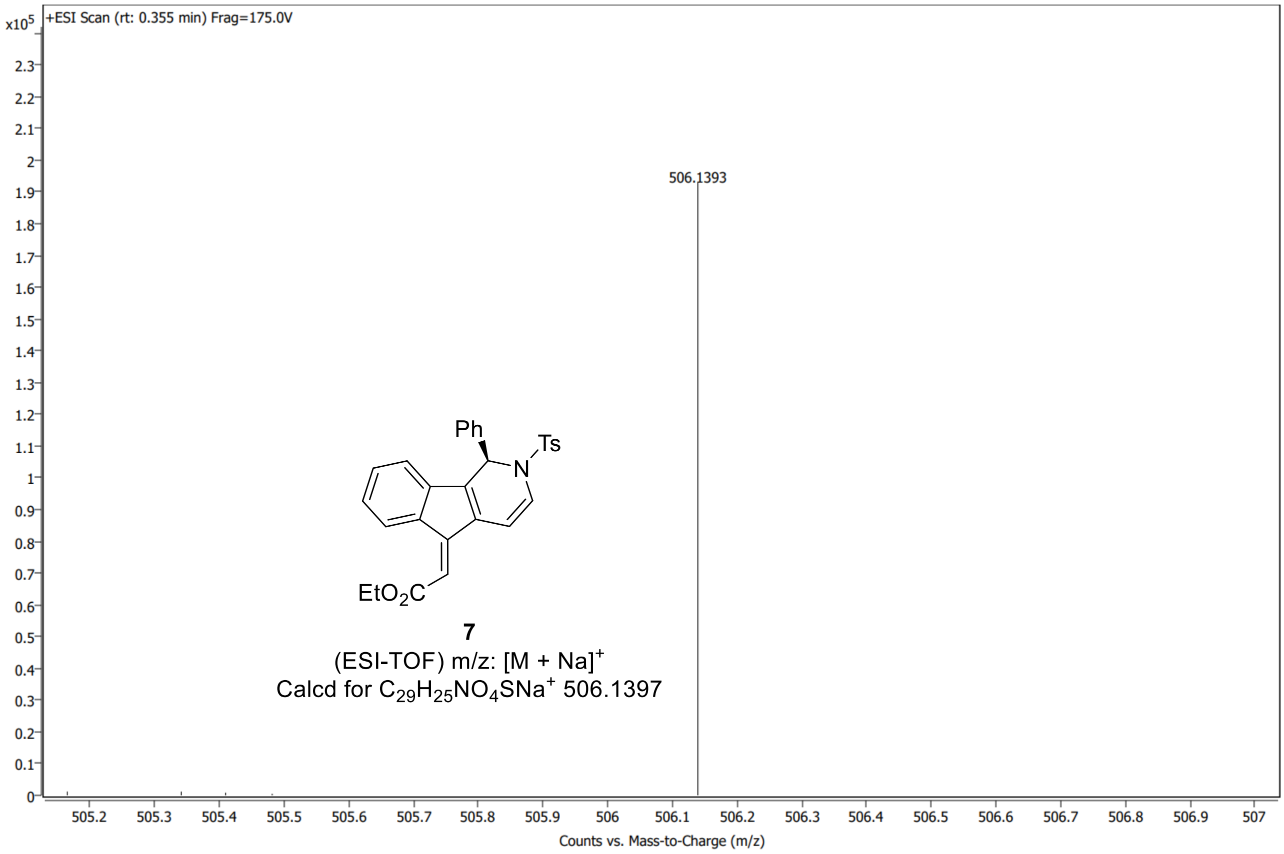
$^{13}$C NMR (100 MHz, CDCl3)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.092 | BV | 0.21 | 213.4077 | 2896.6711 | 49.9280 |
| 7.833 | VB | 0.24 | 191.0196 | 2905.0249 | 50.0720 |
|  |  |  | Totals: | 5801.6960 | 100.0000 |



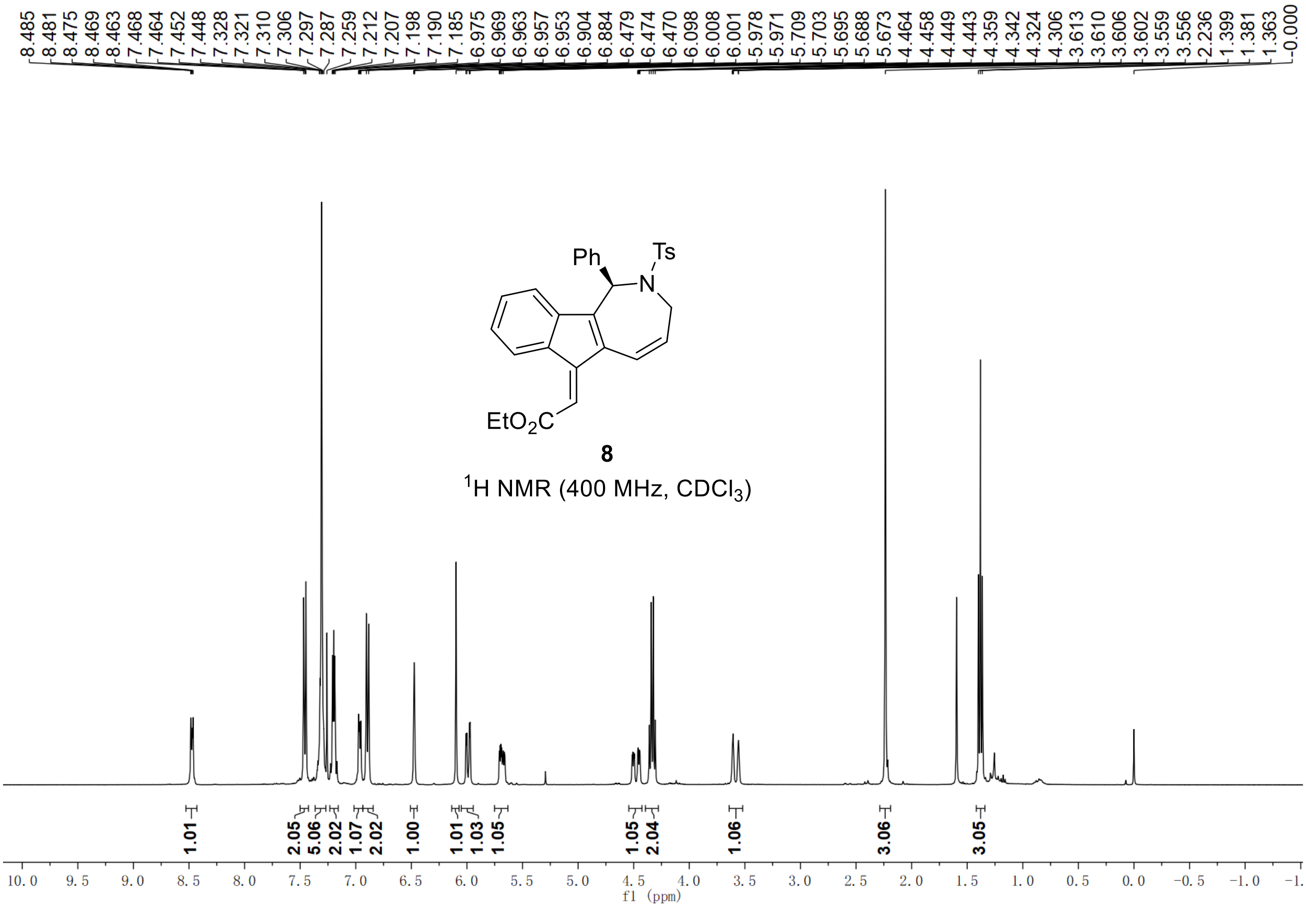
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 7.078 | VB R | 0.21 | 734.9329 | 9703.7949 | 94.4311 |
| 7.822 | BBA | 0.23 | 39.3384 | 572.2648 | 5.5689 |
|  |  |  | Totals: | 10276.0598 | 100.0000 |



**7**

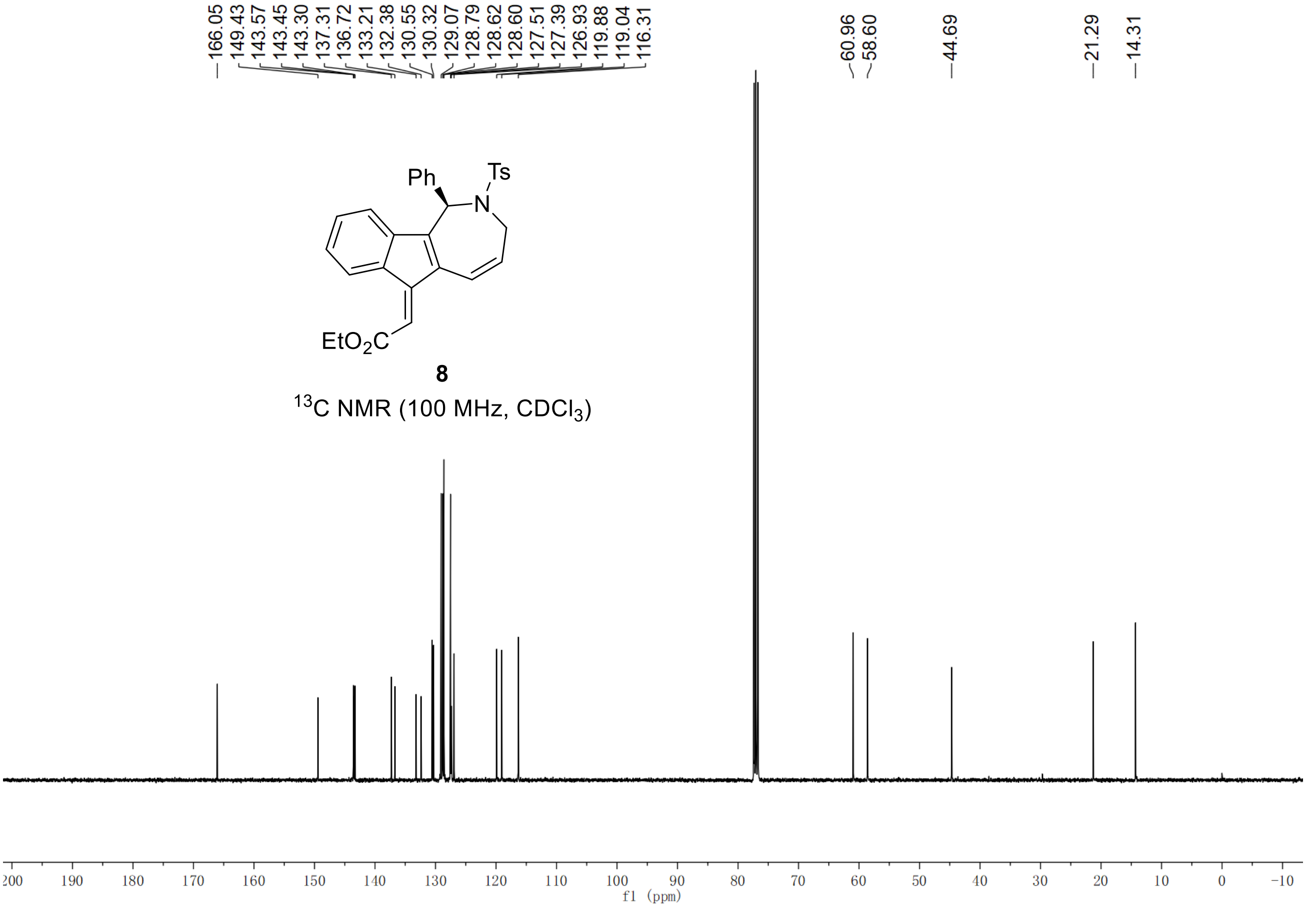
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{29}H_{25}NO_4SNa^+$ 506.1397



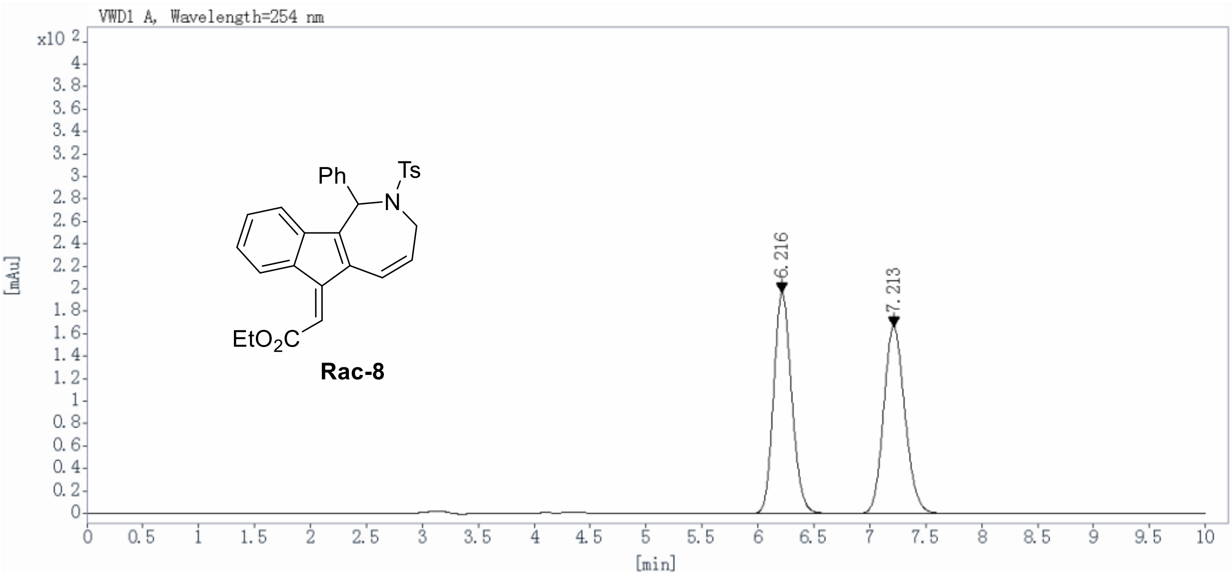
**8**

$^1$H NMR (400 MHz, CDCl$_3$)

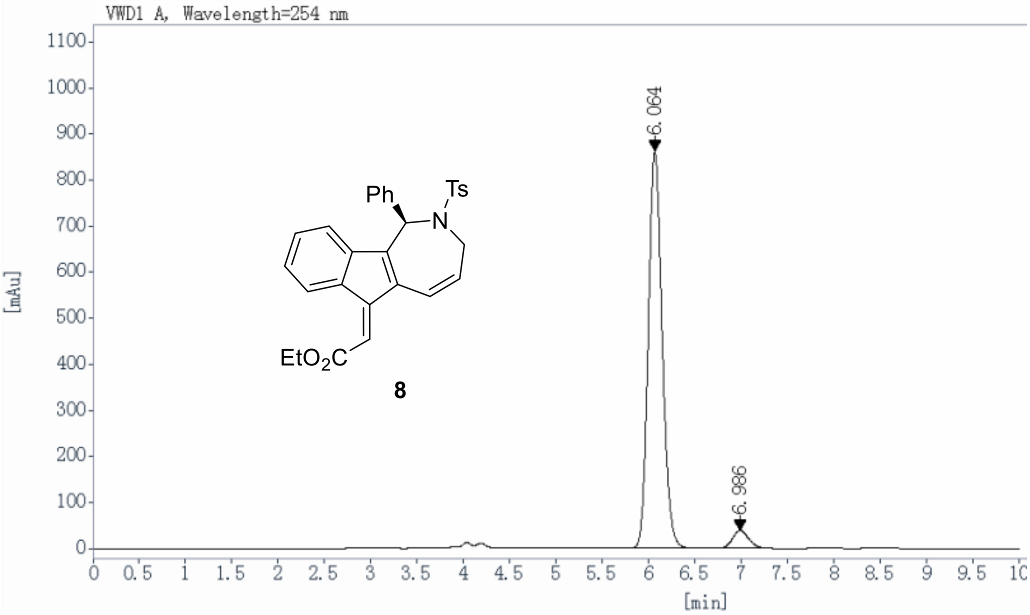


**8**

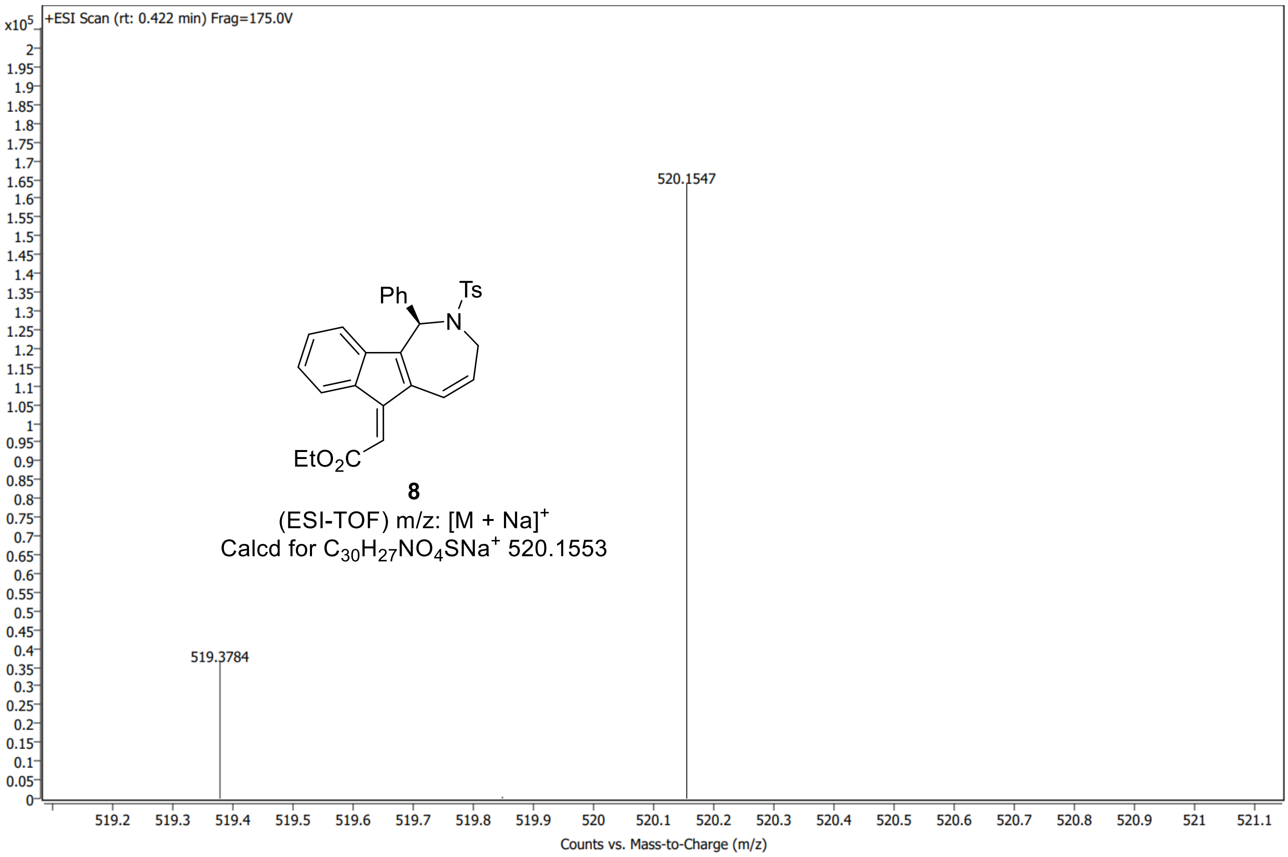
$^{13}$C NMR (100 MHz, CDCl$_3$)



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.216 | VB R | 0.17 | 196.9011 | 2209.7517 | 50.0356 |
| 7.213 | BB | 0.21 | 166.7277 | 2206.6091 | 49.9644 |
| | | | Totals: | 4416.3608 | 100.0000 |



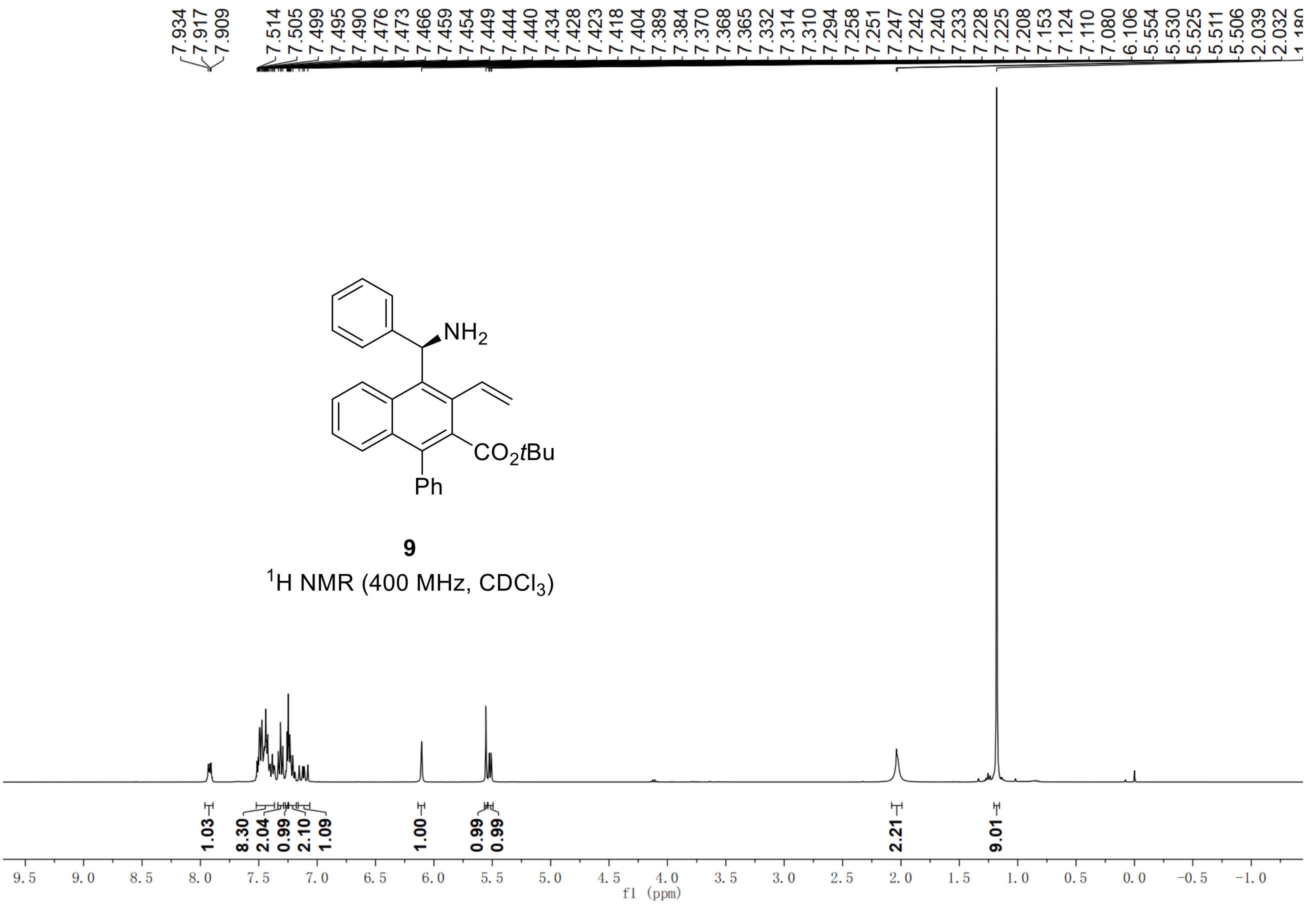
| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 6.064 | VBAR | 0.16 | 862.2455 | 8988.3438 | 95.0923 |
| 6.986 | BBA | 0.19 | 38.3731 | 463.8831 | 4.9077 |
| | | | Totals: | 9452.2268 | 100.0000 |



**8**

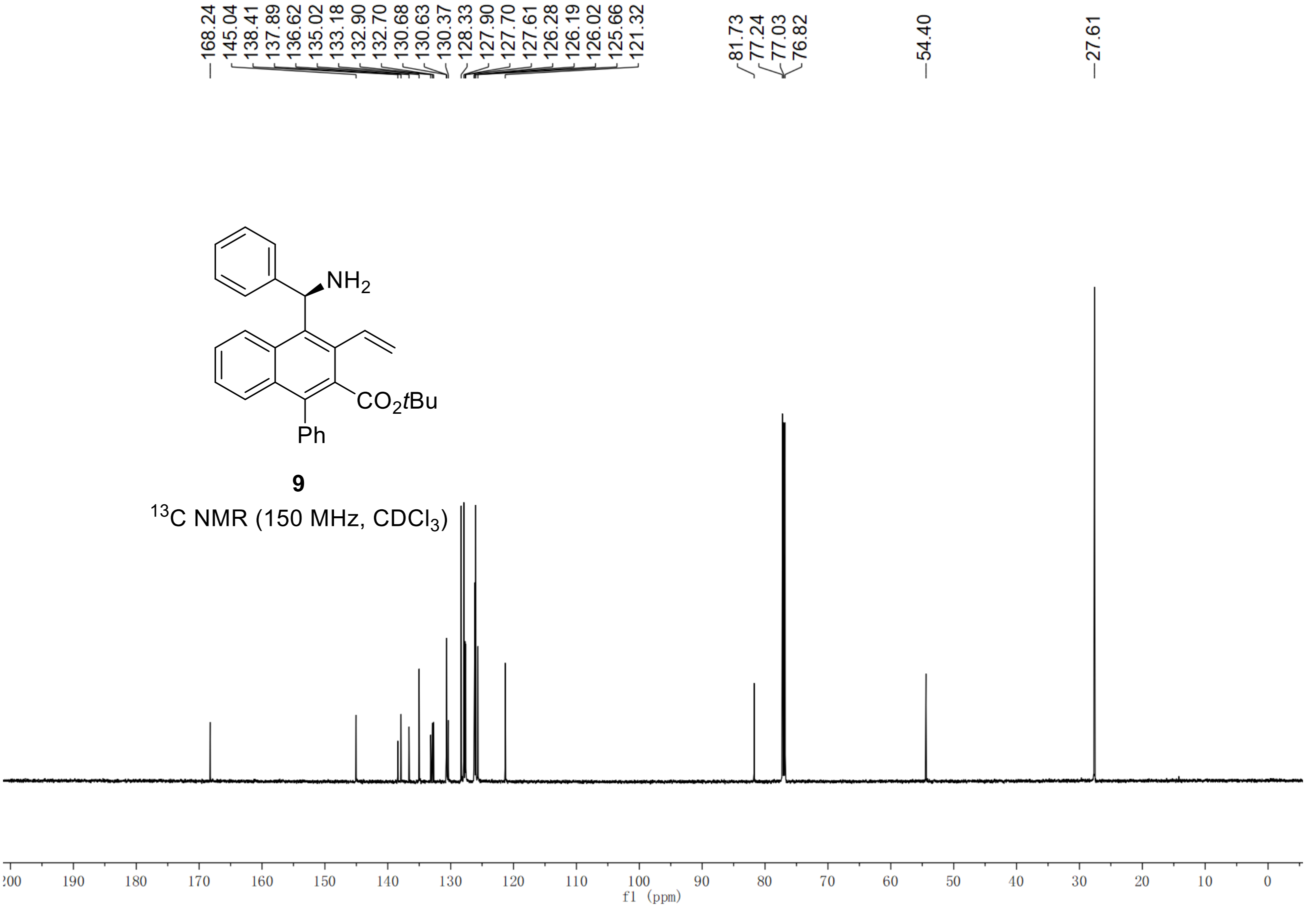
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{30}H_{27}NO_4SNa^+$ 520.1553



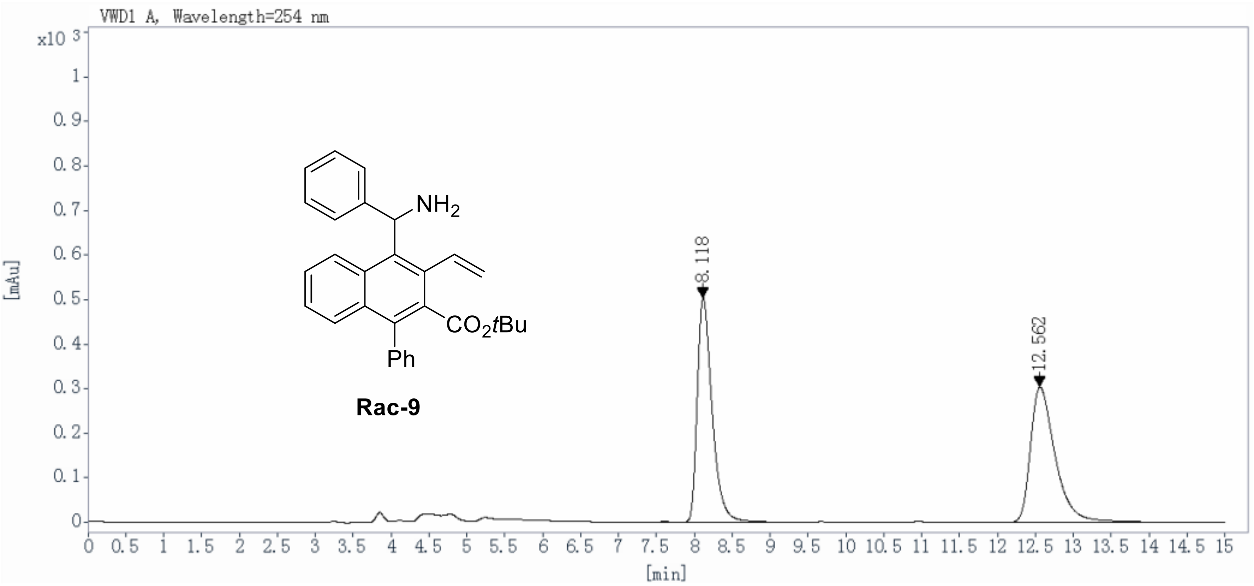
**9**

$^1$H NMR (400 MHz, $CDCl_3$)

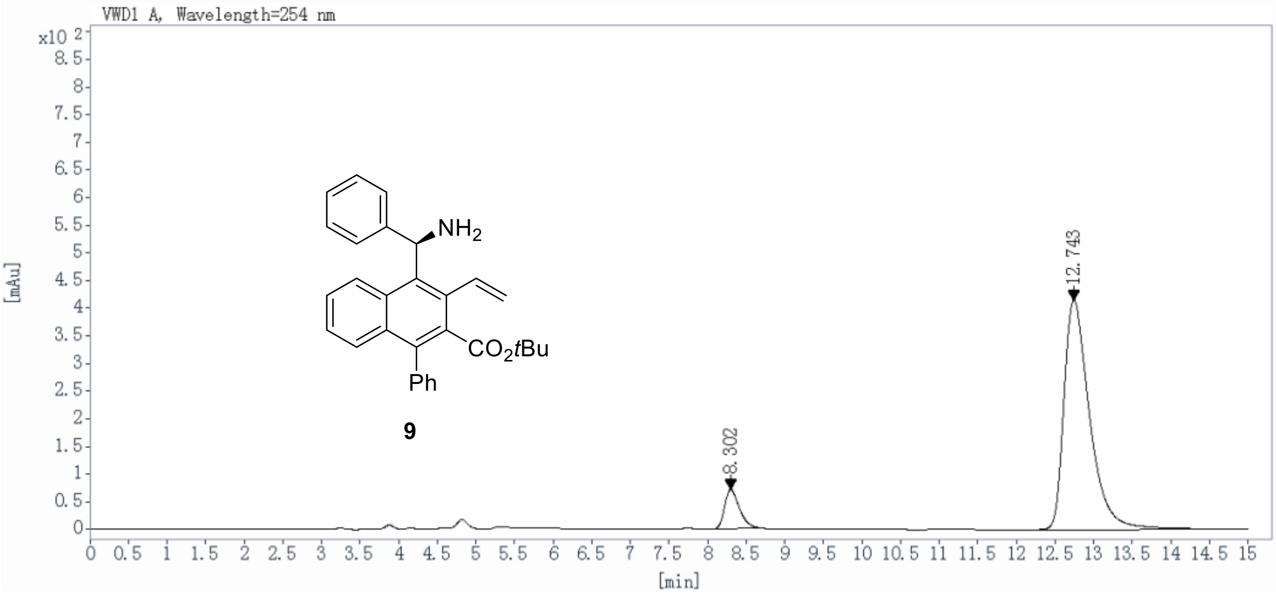


**9**

$^{13}$C NMR (150 MHz, $CDCl_3$)

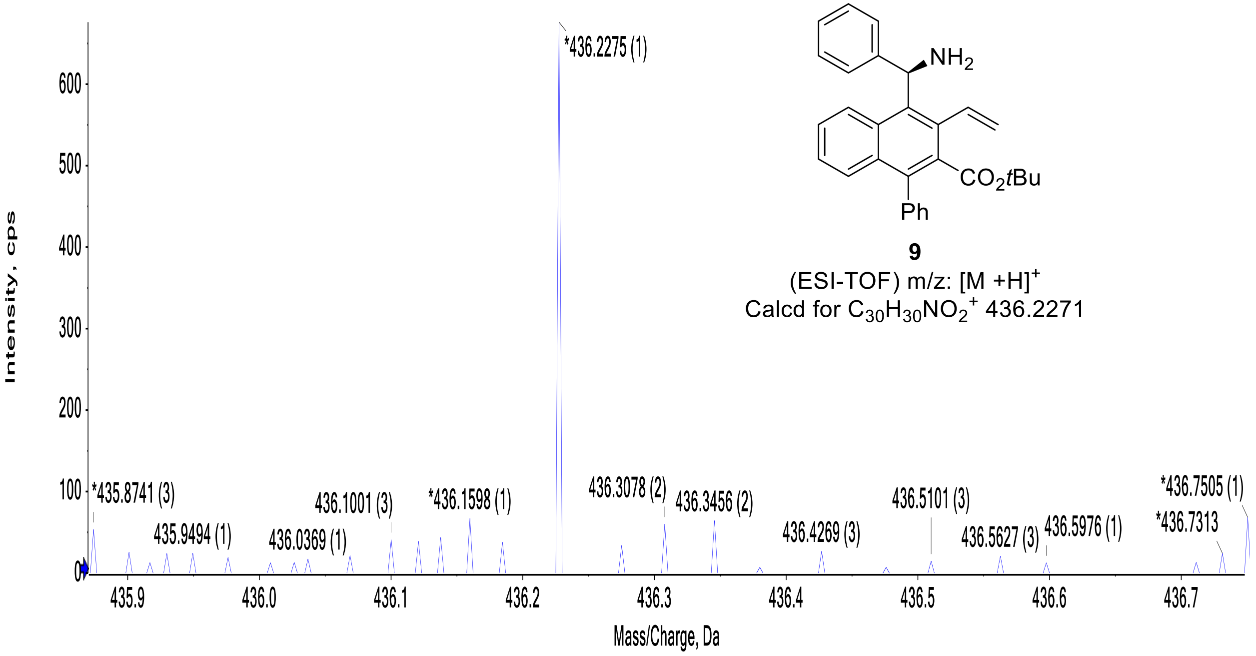


| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.118 | VB R | 0.21 | 505.5327 | 6928.7729 | 49.8832 |
| 12.562 | BBA | 0.35 | 304.3535 | 6961.2271 | 50.1168 |
| | | | Totals: | 13890.0000 | 100.0000 |



| Ret Time [min] | Peak Type | Width [min] | Height [mAU] | Area [mAU*s] | Area [%] |
|---|---|---|---|---|---|
| 8.302 | BBA | 0.21 | 70.9360 | 958.5382 | 9.0040 |
| 12.743 | BBA | 0.36 | 414.9878 | 9687.1885 | 90.9960 |
| | | | Totals: | 10645.7267 | 100.0000 |

Spectrum from 20230510.wiff2 (sample 1) - 1, +TOF MS (300 - 800) from 0.019 to 0.069 min, Recalibrated, centroided



**9**

(ESI-TOF) m/z: [M +H]$^+$

Calcd for $C_{30}H_{30}NO_2^+$ 436.2271